

*The Pearson Guide to*

# Physical Chemistry

for the IIT JEE

- Short-cut methods and problem-solving tricks
- As per the latest IIT JEE format
- Original questions from competitive exams
- Numerous examples and fully solved problems

**Atul Singhal**



**The Pearson Guide to**

# **Physical Chemistry for the IIT JEE**

**ATUL SINGHAL**



Chandigarh • Delhi • Chennai

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**To my grandparents,  
parents and teachers**

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# Preface

*The Pearson Guide to Physical Chemistry for the IIT JEE* is an invaluable book for all the students preparing for the prestigious engineering entrance examination. It provides class-tested course material and problems that will supplement any kind of coaching or resource the students might be using. Because of its comprehensive and in-depth approach, it will be especially helpful for those students who do not have enough time or money to take classroom courses.

- A careful scrutiny of previous years' IIT papers and various other competitive examinations during the last 10 to 12 years was made before writing this book. It is strictly based on the latest IIT syllabus (2009–10) recommended by the executive board. It covers the subject in a structured way and familiarizes students with the trends in these examinations. Not many books in the market can stand up to this material when it comes to the strict alignment with the prescribed syllabus.
- It is written in a lucid manner to assist students to understand the concepts without the help of any guide.
- The objective of this book is to provide this vast subject in a structured and useful manner so as to familiarize the candidates taking the current examinations with the current trends and types of multiple-choice questions asked.
- The multiple-choice questions have been arranged in following categories:

Straight Objective Type Questions (Single Choice), Brainteasers Objective Type Questions (Single Choice), Multiple Correct Answer Type Questions (More than one choice), Linked-Comprehension Type Questions, Assertion-Reason Type Question, Matrix-Match Type Questions and the IIT JEE Corner.

This book is written to pass on to another generation, my fascination with descriptive physical chemistry. Thus, the comments of the readers, both students and instructors, will be sincerely appreciated. Any suggestions for added or updated additional readings would also be welcome.

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I am indebted to my father, B. K. Singhal, mother Usha Singhal, brothers, Amit Singhal and Katar Singh, and sisters, Ambika and Poonam, who have been my motivation at every step. Their never-ending affection has provided me with moral support and encouragement while writing this book.

Last but not the least, I wish to express my deepest gratitude to my wife Urmila and my little,—but witty beyond years, daughters, Khushi and Shanvi who always supported me during my work.

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# CHAPTER 1

# Mole Concept and Stoichiometry

## Chapter Contents

Concept of atoms and molecules, Dalton's atomic theory; Mole concept; Chemical formulae; Chemical equations; Calculations (based on mole concept) involving common oxidation, reduction, neutralization and displacement reactions; Concentration in terms of mole fraction, molarity, molality and normality, and Various levels of multiple-choice questions.

## DALTON'S ATOMIC THEORY

An atom is the smallest particle of an element which is neutral in nature, retains all the properties of the element and takes part in a chemical reaction. The word atom was introduced by Dalton (*alamos* means undivided).

The Dalton's atomic theory was proposed by Dalton on the basis of laws of chemical combination.

### Main Assumptions

- Matter (of any type) is composed of atoms.
- An atom is the smallest, fundamental, undivided particle.
- An atom can neither be created nor destroyed.

- Atoms of an element have similar size, energy and properties while atoms of different element differ in these aspects.
- Atoms combine in whole number ratios to form a molecule, therefore, a molecule is the smallest identity that exists individually.

### Modern view about the atom

According to the modern view:

- An atom is divisible into other smaller particles which are known as subatomic particles. It can also combine in non-whole number ratio as in the case of non-stoichiometric compounds (Berthollide compounds) like  $\text{Fe}_{0.93}\text{O}$ .
- Atoms of same element also differ in mass and mass related properties as in the case of isotopes.

## 1.2 ■ Mole Concept and Stoichiometry

**Molecule** The term molecule was introduced by Avogadro. It is the smallest particle (identity) of matter that can exist independently and retains all the properties of the substance. Normally, the diameter of the molecules is in the range of 4–20 Å and the molecular mass is between 2–1000. In case of macromolecules, the diameter is in the range of 50–250 Å and the molecular weight may be in lakhs.

**Berzelius Hypothesis** According to the Berzelius hypothesis, “Equal volumes of all the gases contain same number of atoms under the similar conditions of temperature and pressure.” This hypothesis on application to law of combining volume confirms that atoms are divisible which is in contrary to Dalton’s theory.

### AVOGADRO’S LAW

- Avogadro’s law explains law of combining volumes.
- According to this law, “Under similar conditions of temperature and pressure, equal volume of gases contain equal number of molecules.”

It means 10 ml of H<sub>2</sub>, O<sub>2</sub>, N or a mixture of gases have same number of molecules.

It is used in:

- (i) Deriving molecular formula of a gas
- (ii) Determining atomicity of a gas
- (iii) Deriving a relation

$$\text{molecular mass} = 2 \times \text{vapour density}$$

$$M = 2 \times V.D.$$

- (iv) Deriving the gram molecular volume

- Avogadro number (N<sup>0</sup> or NA) =  $6.023 \times 10^{23}$ .
- Avogadro number of gas molecules occupy 22.4 litre or 22400 ml or cm<sup>3</sup> volume at STP.
- The number of molecules in 1 cm<sup>3</sup> of a gas at STP is equal to Loschmidt number, that is,  $2.68 \times 10^{19}$
- Reciprocal of Avogadro number is known as Avogram.

### MOLE

- Mole is a unit which represents  $6.023 \times 10^{23}$  particles, atoms, molecules or ions etc., irrespective of their nature.

- Mole is related to the mass of substance, the volume of gaseous substance and the number of particles

$$\text{Mole} = \frac{W}{M}$$

$$= \frac{\text{Wt. of substance in gm.}}{\text{Molar mass of substance (G.m.m)}}$$

Here G.m.m. = Gram molecular mass

$$\text{Mole} = \frac{\text{Volume of substance in litre}}{22.4 \text{ litre}}$$

Volume of one mole of any gas is equal to 22.4 litres of dm<sup>3</sup> at STP. It is known as molar volume.

$$\text{Mole} = \frac{\text{Number of identities}}{\text{Avogadro's number}}$$

$$\text{Mole} = \frac{PV}{RT}$$

Here P = Pressure in atmosphere

V = Volume in litre

T = Temperature in Kelvin

R = Universal gas constant

Relationship of Mole:

A mole of any substance (like N<sub>2</sub>) stands for:

- $6.023 \times 10^{23}$  molecules of N<sub>2</sub>
- $2 \times 6.023 \times 10^{23}$  atoms of nitrogen
- 28 gm of nitrogen
- 22.4 litre of N<sub>2</sub> at STP.

### To Find Total Number of Identities

- Total number of Molecule = mole(n) × N<sub>A</sub>
- Total number of Atoms = mole (n) × N<sub>A</sub> × No. of atoms present in one molecule
- Total number of Electrons = mole (n) × N<sub>A</sub> × No. of electron present in one electron
- Total charge on any ion = mole (n) × N<sub>A</sub> × charge on one ion ×  $1.6 \times 10^{-19}$ C

### Illustrations

1. If a piece of copper weights 0.635 g, how many atoms does it contain?

**Solution** Number of moles of Cu in 0.635 g

$$= \frac{0.635 \text{ g}}{63.5 \text{ g mol}^{-1}} = 10^{-2} \text{ mol}$$

As 1 mole Cu contains  $6.023 \times 10^{23}$  atoms of Cu

$$\begin{aligned} \text{So } 10^{-2} \text{ mole Cu contains } & 6.023 \times 10^{23} \times 10^{-2} \\ & = 6.023 \times 10^{21} \text{ atoms of Cu} \end{aligned}$$

2. Oxygen is present in a one litre flask at a pressure of  $7.6 \times 10^{-10}$  mm of Hg. Calculate the number oxygen molecules in the flask at 0°C.

**Solution**  $PV = nRT$

$$\frac{7.6 \times 10^{-10}}{760} \text{ atm} \times 1 \text{ L}$$

$$= n \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 273 \text{ K}$$

$$n = \frac{7.6 \times 10^{-10} \text{ L atm}}{760 \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 273 \text{ K}}$$

$$= \frac{10^{-12}}{22.41} \text{ mol}$$

Number of molecules

$$= (6.02 \times 10^{23} \text{ mol}^{-1}) (10^{-12}/22.41 \text{ mol})$$

$$= 2.68 \times 10^{10}$$

3. Calculate the total number of electrons present in 1.6 gram of methane.

**Solution** Molecular mass of methane = 16 g mol<sup>-1</sup>

As 16 g CH<sub>4</sub> contains  $6.02 \times 10^{23}$  molecules of CH<sub>4</sub>

So 1.6 g CH<sub>4</sub> contains  $6.02 \times 10^{22}$  molecules of CH<sub>4</sub>

As one molecule of CH<sub>4</sub> contains (6 + 4) = 10 electrons, so  $6.02 \times 10^{22}$  molecules of CH<sub>4</sub> contain  $10 \times 6.02 \times 10^{22}$ .

$$= 6.02 \times 10^{23} \text{ electrons.}$$

4. How many years would it take to spend Avogadro number of rupees at the rate of 10 lac rupees per second?

**Solution** As Avogadro number =  $6.023 \times 10^{23}$

So total rupees =  $6.023 \times 10^{23}$  Rs

Rate of spending = 10 lac rupees/s =  $10^6$  Rs/s

Number of years to spend all the rupees

$$= \frac{6.023 \times 10^{23} \text{ Rs}}{10^6 \times 60 \times 60 \times 24 \times 365 \text{ Rs/year}}.$$

$$= 1.90988 \times 10^{10} \text{ years}$$

5. Calculate the number of atoms of oxygen present in 88 g of CO<sub>2</sub>. What would be the mass of CO having the same number of oxygen atoms?

**Solution** Number of moles of CO<sub>2</sub> =  $\frac{88 \text{ g}}{44 \text{ g mol}^{-1}}$ .

$$= 2 \text{ moles}$$

As one mole of CO<sub>2</sub> contains two moles of oxygen atoms, so two moles of CO<sub>2</sub> contain 4 moles of oxygen atoms.

$$\begin{aligned} \text{Number of oxygen atoms} &= 4 \times 6.023 \times 10^{23} \\ &= 2.5092 \times 10^{24}. \end{aligned}$$

As 1 mole oxygen atom is present in 1 mole of CO so 4 moles oxygen atoms are present in 4 moles of CO. Its mass is  $4(12 + 16) = 112$  g

6. How many atoms of carbon has a young man given to his bride-to-be if the engagement ring contains 0.5 carat diamond? (1 carat = 200 mg)

**Solution** Mass of diamond (C) =  $0.5 \times 200$  mg

$$= 100 \text{ mg} = 100 \times 10^{-3} \text{ g} = 0.1 \text{ g}$$

$$\text{Number of mole of C} = \frac{0.1 \text{ g}}{12 \text{ g mol}^{-1}}.$$

$$= 1/120 \text{ mole}$$

$$\begin{aligned} \text{Number of C atoms} &= \frac{1}{120} \times 6.023 \times 10^{23} \\ &= 5.02 \times 10^{21} \end{aligned}$$

7. If the Faraday were to be 60230 coulombs instead of 96500 coulombs, what will be the charge on an electron?

**Solution** One mole electron carries 1 Faraday charge.

As  $6.023 \times 10^{23}$  electrons carry = 60230 C

$$\begin{aligned} \text{So 1 electron carries} & \frac{60230}{6.023 \times 10^{23}} \text{ C} \\ & = 1 \times 10^{-19} \text{ C.} \end{aligned}$$

## MASS

Mass can be expressed in terms of atoms or molecules as follows:

### Atomic Mass

It is the relative mass of an atom which shows how many times an atom is heavier than 1/12 mass of C-12.

- The atomic mass of any element expressed in grams is called G.A.M. (gram atomic mass).

$$\text{Atomic mass} = E \times V$$

Here E = Equivalent weight

V = Valency

- Atomic mass =  $\frac{6.4}{\text{Specific Heat in cal.}}$

It is known as Dulong Petit's law.

### REMEMBER

Gram atomic weight is atomic weight expressed in grams but it has a special significance with reference to a mole.

### Molecular Mass

Molecular mass represents the total mass of a molecule, that is, number of times a molecule is heavier than that of 1/12 weight of C-12.

- It is non-variable.
- It is now called relative molecular mass.

### Determination of Molar Mass

It is possible by these methods

### Vapour Density Method

Vapour density of a gas is defined as the ratio of the weight of a certain volume of the gas to the weight of the same volume of hydrogen at the same temperature and pressure.

Vapour density of a gas

$$= \frac{\text{Weight of 'V' litres of the gas}}{\text{Weight of 'V' litres of H}_2 \text{ at the same temperature and pressure}}$$

Suppose 'V' litres of the gas contains 'n' molecules.

Vapour density of gas

$$= \frac{\text{Weight of 'n' molecules of the gas}}{\text{Weight of 'n' molecules of H}_2}$$

$$= \frac{\text{Weight of 1 molecule of the gas}}{\text{Weight of 1 molecule of H}_2}$$

$$= \frac{1}{2} \times \frac{\text{Weight of 1 molecule of the gas}}{\text{Weight of 1 atom of H}_2}$$

$$\text{V.D.} = \frac{W \times 22400}{\text{Volume at STP (in ml)}}$$

Here W = Weight of substance in gm.

Molecular mass =  $2 \times \text{Vapour density}$

### Graham Diffusion Method

$$r_1/r_2 = \sqrt{(M_2/M_1)}$$

Here  $r_1$ ,  $r_2$  are rates of diffusion for two species while  $M_1$ ,  $M_2$  are their molecular masses respectively.

- By Colligative Properties Methods:

$$\pi V = \frac{W}{m} RT$$

Here  $\pi$  = Osmotic pressure in atm.

V = Volume in litre

W = Weight in grams

R = Universal gas constant

T = Given temperature

m = Molar mass

### Illustrations

- The weight of one litre sample of ozonized oxygen at NTP was found to be 1.5 g. When 100 ml of this mixture at NTP were treated with terpine oil, the volume was reduced to 90 ml. Hence calculate the molecular weight of ozone.

**Solution** Volume absorbed by terpine oil = 10 ml

As volume of ozone = 10 ml (as terpine oil absorbed  $O_3$ )

So Volume of  $O_2$  =  $100 - 10 = 90$

Mol. wt. of ozonized oxygen

$$= \frac{WRT}{PV} = \frac{1.5 \times 0.0821 \times 273}{1 \times 1}$$

$$= 33.62$$

As volume or mole ratio of  $O_2$  and  $O_3$  is 900 : 100

So mol. wt. of ozonized oxygen

$$= \frac{900 \times 32 + 100 \times X}{1000}$$

$$33.62 = \frac{900 \times 32 + 100 \times X}{1000}$$

$$X = 48.2$$

Hence mol. wt. of ozone = 48.2

## Equivalent Weight

- Equivalent weight is the weight of an element or a compound which combines with or displaces 1.008 part by weight of  $H_2$  or 8 part by weight of  $O_2$  or 35.5 part by weight of  $Cl_2$ .
- Equivalent weight is a number and when it is denoted in grams, it is called gram equivalent.
- It depends upon the nature of chemical reaction in which substance takes part.

## Methods to Find Equivalent Weight

### (i) For Acids

$$E = \frac{\text{Molecular weight}}{\text{Protocuity or Basicity of Acid}}$$

For example, for  $H_3PO_4$ , E = M/3

For  $H_2SO_4$ , E = M/2

### (ii) For Bases

$$E = \frac{\text{Molecular weight}}{\text{Acidity or number of } OH^- \text{ ions}}$$

For example, for  $Ca(OH)_2$ , E = M/2

For  $Al(OH)_3$ , E = M/3

### (iii) For Ions

$$E = \frac{\text{Molecular weight}}{\text{Charge on ion}}$$

For example, for  $SO_4^{2-}$ , E = M/2

For  $PO_4^{3-}$ , E = M/3

### (iv) For Compounds

$$E = \frac{\text{Molecular weight}}{\text{Valency of cation or anion}}$$

For example, for  $CaCO_3$ , E = M/2

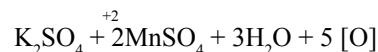
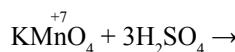
$AlCl_3$ , E = M/3

### (v) For Redox Reactions

$$E = \frac{\text{Molecular weight}}{\text{Change in oxidation number}}$$

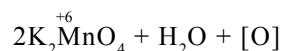
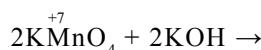
For example, for  $KMnO_4$

(a) In acidic medium: E = M/5



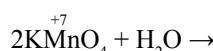
5 unit change in oxidation number.

(b) In basic medium: E = M/1



one unit change in oxidation number

(c) In neutral medium: E = M/3

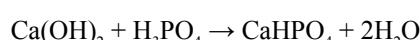


3 unit change in oxidation number

### (vi) For Acidic Salt

$$E = \frac{\text{Molecular weight}}{\text{Number of replaceable H-atoms}}$$

For example, for  $H_3PO_4$



$$E = M/2$$

## 1.6 ■ Mole Concept and Stoichiometry

### (vii) Some other methods

#### (a) Hydrogen displacement method

$$E = \frac{w \times 11200}{\text{Volume of H}_2 \text{ at NTP}}$$

#### (b) Oxide formation method

$$E = \frac{\text{Wt. of metal}}{\text{Wt. of oxygen}} \times 8$$

$$\text{Weight of oxygen} = \text{weight of metal oxide} - \text{weight of metal}$$

#### (c) Chloride formation method:

$$E = \frac{\text{Wt of metal}}{\text{Wt. of chloride}} \times 35.5$$

$$\text{Weight of chloride} = \text{weight of metal chloride} - \text{weight of metal}$$

#### (d) Double decomposition methods

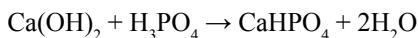
$$\frac{\text{Eq. wt. of salt taken}}{\text{Eq. wt. of salt ppt.}} = \frac{\text{Wt. of salt taken}}{\text{Wt. of salt ppt.}}$$

#### (e) Metal displacement methods

$$\frac{E_1}{E_2} = \frac{W_1}{W_2}$$

## Illustrations

9. Find the equivalent mass of  $\text{H}_3\text{PO}_4$  in the reaction:



**Solution** As in this reaction only two hydrogen atoms are replaced so its equivalent mass will be given by the following expression:

Equivalent mass of  $\text{H}_3\text{PO}_4$

$$= \frac{\text{Molecular mass of H}_3\text{PO}_4}{2}$$
$$= \frac{98}{2} = 49$$

10. On heating 0.199 g of a metallic oxide in a current of hydrogen 0.045 g of water is formed. Find the equivalent weight of the metal.

**Solution** Weight of Metallic oxide = 0.199 g

As 16 g oxygen is present in = 18 g  $\text{H}_2\text{O}$

$$\text{So O}_2 \text{ present in } 0.045\text{g H}_2\text{O} = \frac{16 \times 0.045}{18}$$
$$= 0.04 \text{ g}$$

$$\text{Weight of metal} = 0.199 - 0.04$$

$$= 0.159$$

$$\text{Equivalent weight of metal} = \frac{0.159 \times 8}{0.04}$$

$$= 31.8$$

11. 4.215 g of a metallic carbonate was heated in a hard glass tube and the  $\text{CO}_2$  evolved was found to measure 1336 ml at 27°C and 700 mm pressure. What is the equivalent weight of the metal?

**Solution** Metallic carbonate  $\rightarrow$  metallic oxide +  $\text{CO}_2$

$$\text{Wt. of CO}_2 = \frac{44 \times 1120}{22400}$$

$$= 2.2 \text{ g}$$

$$\text{Wt. of metallic oxide} = 4.125 - 2.2 = 2.015 \text{ g}$$

$$\text{By law of equivalent : } \frac{E + \text{CO}_3^{2-}}{E + \text{O}^{2-}}$$

$$= \frac{4.125}{2.015}$$

$$\text{Hence, E (eq. wt. of metal)} = 12.58$$

## Chemical Formula

A chemical formula represents the combination of atoms of all the elements which makes up a compound. It represents the relative ratio of atoms of its constituent elements. In case of a compound, it represents one molecule, one mole, one gram molecular weight of the compound Example,  $\text{S}_8$  represents one molecule of phosphorous and one mole of phosphorous.

Example,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  represents one molecule, one mole and one gram molecular weight of hydrated copper sulphate.

## Empirical and Molecular Formulas

### Empirical Formula

It gives the simplest ratio of the number of atoms of different elements present in one molecule of a compound. It does not represent the actual number of atoms of different elements present in one molecule of the compound.

**Calculation of the Empirical Formula:** It involves the following steps, one by one:

- (i) First determine the percentage composition by weight of each element present in the compound.

$$C \% = \frac{12}{44} \times \frac{\text{wt. of CO}_2}{\text{wt. of organic comp.}} \times 100$$

$$H \% = \frac{2}{18} \times \frac{\text{wt of H}_2\text{O}}{18 \text{ wt. of org. comp.}} \times 100$$

### Duma's method

$$N \% = \frac{28}{22400} \times \frac{\text{Volume of N}_2 \text{ at S.T.P.}}{\text{wt. of Org. comp.}} \times 100$$

OR

$$N \% = \frac{\text{Vol of N}_2 \text{ at S.T.P.}}{8 \times \text{Wt of Org comp.}}$$

### Kjeldahl's Method

$$N \% = \frac{1.4 \times N \times V}{\text{Wt. of org. compound}}$$

Here N = normality of acid the used to neutralize ammonia

V = volume of acid the used to neutralize ammonia

- (ii) Now the percentage of each element is divided by its atomic weight to get the relative number of atoms of each element.
- (iii) These relative numbers obtained are divided by smallest number to get the simplest ratio numbers.
- (iv) If the simplest ratio number is not a whole number it should be multiplied by a suitable integer to get a whole number.
- (v) The ratio of these simple whole numbers gives the empirical formula of the compound.

### Molecular Formula

It shows the actual number of atoms of different elements present in one molecule of the compound.

$$\blacksquare n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}}$$

- Molecular formula = empirical formula  $\times$  n.

- Molecular weight of a substance can be determined by methods like Vapour density method, Elevation in boiling point method, Depression in freezing point methods etc.
- The molecular weight of volatile compounds is determined by Victor Mayer's method.
- Molecular Weight =  $2 \times$  Vapour density
- Molecular weight = empirical formula wt.  $\times$  'n'.
- For some compounds the molecular formula and empirical formula may be same also.

### Illustrations

12. A certain organic compound was found to contain 33.6 % C, 5.6 % H and 49.6 % chlorine. Find the empirical formula of the organic compound.

### Solution

Element	%	Atomic ratio	Simplest Ratio
C	33.8	$33.8/12 = 2.8$	$2.8/0.7 = 4$
H	5.6	$5.6/1 = 5.6$	$5.6/0.7 = 8$
Cl	49.6	$49.6/35.5 = 1.4$	$1.4/0.7 = 2$
O	11.0	$11/16 = 0.7$	$0.7/0.7 = 1$
Thus $\text{C}_4\text{H}_8\text{Cl}_2\text{O}$ is the empirical formula of the compound.			

13. A well-known antibiotic penicillin, contains C 57.49 %, H 5.39 %, N 8.39 %, S 9.58 %; the remainder being oxygen. Given that penicillin contains one atom of sulphur per molecule, calculate the molecular formula of the antibiotic.

### Solution

$$\% \text{ C} = 57.49$$

$$\% \text{ H} = 5.39$$

$$\% \text{ N} = 8.39$$

$$\% \text{ S} = 9.58$$

$$\begin{aligned} \% \text{ O} &= 100 - (57.49 + 5.39 + 8.39 + 9.58) \\ &= 19.15 \end{aligned}$$

Empirical formula

## 1.8 ■ Mole Concept and Stoichiometry

Element	%	Relative no. of atoms	Simplest Ratio
C	57.49	$57.49/12 = 4.79$	16
H	5.39	$5.39/1 = 5.39$	18
N	8.39	$8.39/14 = 0.599$	2
S	9.58	$9.58/32 = 0.299$	1
O	19.15	$19.15/16 = 1.196$	4
Empirical formula is $C_{16}H_{18}N_2SO_4$			

As the given antibiotic contains only one atom of sulphur per molecule. The calculated empirical formula  $C_{16}H_{18}N_2SO_4$ , contains only one atom of sulphur. Hence the same is the molecular formula of the antibiotic.

14. A compound has molar mass of 147 g. It contains 49 % C and 2.72 % H. On Carius estimation, 2.561 mg of the compound gave 5 mg of AgCl. Find the empirical and molecular formula.

### Solution

Element	%	Atomic ratio	Simplest Ratio
C	49	$49/12 = 4.1$	3
H	2.72	$2.72/1 = 2.72$	2
Cl		$\frac{(35.5/143.5) \times 5 \times 100}{2.581}$	
		$= 47.9 \quad 47.9/35.5 = 1.34$	1
		$C_3H_2Cl$	is the empirical formula.
		$n = 147/73.5 = 2$	
		The molecular formula is $C_6H_4Cl_2$ .	

15. Methyl orange, an acid-base indicator, is the sodium salt of an acid that contains C, H, N, S and O. Quantitative analysis gave 51.4 % C, 4.3 % H, 12.8 % N, 9.8 % S and 7.0 % Na. What is the empirical formula of methyl orange?

### Solution

% C = 51.4

$$\% H = 4.3$$

$$\% N = 12.8$$

$$\begin{aligned}\% S &= 9.8 \\ \% Na &= 7.0 \\ \% O &= 14.7\end{aligned}$$

Element	%	Relative no. of atoms	Simplest Ratio
C	51.4	$51.4/12 = 4.28$	14
H	4.3	$4.3/1 = 4.3$	14
N	12.8	$12.8/14 = 0.914$	3
S	9.8	$9.8/32 = 0.306$	1
Na	7.0	$7/23 = 0.304$	1
O	14.7	$14.7/16 = 0.918$	3
So empirical formula is $C_{14}H_{14}N_3SO_3Na$			

### Expression of Concentration of Solution

The solution whose concentration is exactly known is referred as standard solution and such solutions are prepared in volumetric or standard flask.

### Concentration

It is the amount of solute present in one litre of solution. It is denoted by C or S.

$$C \text{ or } S = \frac{\text{Weight of solute in gram}}{\text{Volume in litre}}$$

$$C = N \times E$$

Here N = normality

$$E = \text{Eq. wt.}$$

### Molarity

It is the number of moles or gram moles of solute dissolved per litre of the solution. Molarity is denoted by 'M'.

$$M = \frac{\text{Weight of solute in gram}}{\text{Molar mass} \times \text{volume in litre}}$$

- When molarity of a solution is one, it is called a molar solution. and when it is 0.1, solution is called decimolar solution.

- Molarity depends upon temperature and its unit is mol/litre.

$$M_1 V_1 = M_2 V_2$$

- On dilution water added =  $V_2 - V_1$

- When the solution of two different substances react together then

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

Here M, V, n are molarity, volume and number of molecules taking part in a reaction respectively.

- When a mixture of different solutions having different concentrations are taken the molarity of the mixture is calculated as follows:

$$M = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2} \dots\dots\dots$$

- When density and % by weight of a substance in a solution are given molarity is find as follows:

$$M = \frac{\% \text{ by weight} \times d \times 10}{\text{Molecular weight}}$$

Here d = density

## Molality

It is the number of moles or gram moles of solute dissolved per kilogram of the solvent. It is denoted by 'm'.

$$m = \frac{\text{Weight of solute in gram}}{\text{Molar mass} \times \text{wt. of solvent in Kg}}$$

- If molality is one solution, it is called molal solution.
- One molal solution is less than one molar solution.
- Molality is preferred over molarity during experiments as molality is temperature independent while molarity is temperature dependent.

## Normality

It is the number of gram equivalents of solute present in one litre of the solution and it is denoted by 'N'.

$$N = \frac{\text{Weight of solute in gram}}{\text{Equivalent mass} \times \text{volume in litre}}$$

- When normality of a solution is one, the solution is called normal solution and when it is 0.1, the solution is called deci-normal solution.

## Normality Equation

$$N_1 V_1 = N_2 V_2$$

- Volume of water added =  $V_2 - V_1$

Here  $V_2$  = volume after dilution

$V_1$  = volume before dilution

- When density and % by weight of a substance in a solution are given normality is find as follows:

$$N = \frac{\% \text{ by weight} \times d \times 10}{\text{Equivalent weight}}$$

Here d = density of solution

- When a mixture of different solutions having different concentrations are taken the normality of the mixture is calculated as follows:

$$N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2} \dots\dots\dots$$

- In case of acid base neutralization the normality of the resulting solution

$$N = \frac{N_1 V_1 - N_2 V_2}{V_1 + V_2}$$

- To find weight of substance

$$W = \frac{NEV}{1000}$$

## Relation between Normality and Molarity

$N \times \text{Eq wt.} = \text{molarity} \times \text{molar mass}$

$N = \text{molarity} \times \text{valency}$

$N = \text{molarity} \times \text{number of H}^+ \text{ or OH}^- \text{ ion.}$

## Mole fraction

It is the ratio of moles of one component to the total number of moles present in the solution. It is expressed by X for example, for a binary solution two component A and B.

$$X_A = \frac{n_A}{n_A + n_B} .$$

$$X_B = \frac{n_B}{n_A + n_B} .$$

$$X_A + X_B = 1$$

## 1.10 ■ Mole Concept and Stoichiometry

$$\text{Mole fraction of solute } (X_A) = \frac{n_2}{n_1 + n_2} .$$

or

$$X_2$$

Here  $n_1$ ,  $n_2$  represent moles of solvent and solute respectively.

Mole fraction does not depend upon temperature as both solute and solvent are expressed by weight.

### Illustrations

16. Calculate the volume of water to be added to a 100 ml of 5N solution to make it 0.01 N.

**Solution** According to normality equation,

$$N_1 V_1 = N_2 V_2$$

$$0.01 \times V_1 = 5 \times 100$$

$$V_1 = \frac{5 \times 100}{0.01} = 50000 \text{ ml}$$

So volume of water to be added

$$= 50000 - 100$$

$$= 49900 \text{ ml}$$

$$= 49.9 \text{ l}$$

17. 10 ml of 0.02 M  $\text{KMnO}_4$  is required to oxidize 20 ml of oxalic acid of certain strength. 25 ml of the same oxalic acid is required to neutralize 20 ml of NaOH of unknown strength. Find the amount of NaOH in a litre of the solution.

(Molecular weight of NaOH = 40)

**Solution** In acidic medium

$$1 \text{ M } \text{KMnO}_4 = 5 \text{ N } \text{KMnO}_4$$

$$0.02 \text{ M } \text{KMnO}_4 = 0.1 \text{ N } \text{KMnO}_4$$

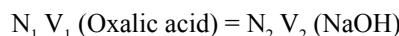
According to normality equation,

$$N_1 V_1 (\text{KMnO}_4) = N_2 V_2 (\text{Oxalic acid})$$

$$0.1 \times 10 = N_2 \times 20$$

$$N_2 = \frac{10 \times 0.1}{20} = 0.05 \text{ N}$$

Again



$$0.05 \times 25 = N_2 \times 20$$

$$N_2 = \frac{0.05 \times 25}{20} = 0.0625 \text{ N}$$

$$\text{As } S = N \times E$$

$$\text{So } S = 0.0625 \times 40 = 2.5 \text{ g L}^{-1}$$

18. The formula weight of an acid is 82.0 100 cm<sup>3</sup> of a solution of this acid containing 39.0 g of the acid per litre were completely neutralized by 95.0 cm<sup>3</sup> of aqueous NaOH containing 40.0 g of NaOH per litre. What is the basicity of the acid?

**Solution** Normality of acid =  $\frac{39}{82/n \times 1}$

$$\text{Normality of NaOH} = \frac{40}{40} \times \frac{1000}{1000} = 1$$

Now, Mew. of acid = Meq. of NaOH

$$\frac{39 n}{82} \times 100$$

$$= 1 \times 95$$

So  $n = 2$ ; Hence here acid is dibasic.

19. What volume at NTP of ammonia gas will be required to be passed into 30 ml of  $\text{H}_2\text{SO}_4$  solution bring down the acid normality to 0.2 N?

**Solution** Meq. of original  $\text{H}_2\text{SO}_4 = 30 \times 1 = 30$

Meq. of  $\text{H}_2\text{SO}_4$  after passing  $\text{NH}_3 = 30 \times 0.20 = 6$

Meq. of  $\text{H}_2\text{SO}_4$  lost =  $30 - 6 = 24$

Meq. of  $\text{NH}_3$  passed = Meq. of  $\text{H}_2\text{SO}_4$  lost

$$\frac{w}{17} \times 1000 = 24$$

$$w_{\text{NH}_3} = 0.408 \text{ g}$$

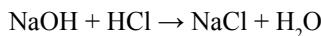
$$\text{Volume of } \text{NH}_3 \text{ at STP} = \frac{22.4 \times 0.408}{17}$$

$$= 0.5376 \text{ litre}$$

$$= 537.6 \text{ ml}$$

20. What volume of a solution of hydrochloric acid containing 73 g of acid litre would suffice for

the exact neutralization of sodium hydroxide obtained by allowing 0.46 g of metallic sodium to act upon water?



Thus, meq. of Na = Meq. of NaOH formed = Meq. of HCl used

$$\frac{0.46}{23} \times 1000 = \frac{73}{36.5} \times V$$

$$(\text{Meq. of HCl} = N \times V)$$

$$= 10 \text{ ml}$$

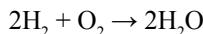
## Limiting Reagent

When two reagents or reactants react to give various product then the number of moles of product form according to the reagent or reactant which is completely consumed during the reaction. The reagent or reactant which is completely consumed during the reaction is called limiting reagent that is, the reagent which gives the least number of moles of the product is called limiting reagent.

## Illustrations

21. 2 g  $\text{H}_2$  reacts with 10 g  $\text{O}_2$  to form water. How much water is formed?

**Solution** Hydrogen reacts with oxygen as follows:



$$\text{Number of moles of H}_2 = \frac{2}{2} = 1 \text{ moles}$$

$$\text{Number of moles of O}_2 = \frac{10}{32} = 0.3125 \text{ moles}$$

As 2 moles of  $\text{H}_2$  reacts with 1 mole of  $\text{O}_2$  to form 2 moles of  $\text{H}_2\text{O}$  so, for 1 mole of  $\text{H}_2$  only 0.3125 moles of  $\text{O}_2$  is present. Thus  $\text{O}_2$  is the limiting reagent here.

As 1 mole of  $\text{O}_2$  gives 2 moles of  $\text{H}_2\text{O}$ .

So 0.3125 mole of  $\text{O}_2$  gives  $\frac{2}{1} \times 0.3125$

= 0.625 moles of  $\text{H}_2\text{O}$

Weight of  $\text{H}_2\text{O}$  formed = Moles  $\times$  Mol. weight

$$= 0.625 \times 18$$

$$= 11.25 \text{ g H}_2\text{O}$$

## Chemical Equations and Numerical Calculations

- A balanced chemical reaction represents a stoichiometric equation.
- In a stoichiometric equation, the coefficient of reactants and products represents their stoichiometric amounts.
- The reactant which is completely used during an irreversible reaction is called limiting reagent while the reactant left is called excess reagent.

For example, if 20 g of calcium is burnt in 32 g of  $\text{O}_2$  then Ca is limiting reagent while  $\text{O}_2$  is excess reagent.

- Stoichiometric calculations help in finding whether the production of a particular substance is economically cheap or not.
- These stoichiometric calculations are of following four types:
  - Calculations based on weight: weight relationship
  - Calculations based on weight: volume relationships.
  - Calculations based on volume: volume relationships
  - Calculations based on weight: volume – energy relationships
- If the amount of the reactant in a particular reaction is known, then the amount of the other substance needed in the reaction or the amount of the product formed in the reaction can be found out.
- For stoichiometric calculations, the following steps must be considered:
  - A balanced chemical equation using chemical formulas of reactants and products must be written.
  - Here the coefficients of balanced chemical equation provide the mole ratio of the reactants and products.
  - This mole ratio is convertible into weight – weight ratio (w/W), weight – volume (w/V) ratio or volume – volume (v/V) ratio. These are called percentage by weight, percentage by volume and percentage by strength respectively.

## Gravimetric Analysis

It is an analytical technique based on the measurements of mass of solid substances or the volume of the gaseous species. It is also divided into three categories:

- (i) Mass-Mass (weight-weight) relation
- (ii) Mass-Volume relation
- (iii) Volume-Volume relation

### (i) Problems Involving Mass-Mass or Weight-Weight Relationship

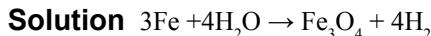
This relationship relates the mass of a reactant or product with the mass of another reactant or product.

For solving such problems, one should proceed according to the following instructions given below:

- First, write down the balanced equation to represent the chemical change.
- Now write the number of moles below the formula of the reactants and product. We must also write the relative weights of the reactants and products (which are calculated from the respective molecular formula) below the respective formula.
- Finally, apply the unitary method to calculate the unknown factor(n or s).

## Illustrations

22. Find weight of iron which will be converted into its oxide by the action of 18 g of steam on it.



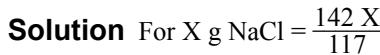
$$3 \times 56 \quad 4 \times 18$$

As by 72 g steam the weight of Fe oxidized = 168 g

So by 18 g " " " "

$$= \frac{168 \times 18}{72} = 72 \text{ g}$$

23. 0.9031 g of NaCl and KCl on reaction with  $\text{H}_2\text{SO}_4$  gave 1.0784 g of a mixture of  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ . Find the percentage composition of the compound.



$$\text{For } (0.9031 - X) \text{ g KCl} = \frac{174}{149} (0.9031 - X)$$

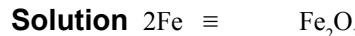
that is,  $\frac{142}{117} X + \frac{174}{149} (0.9031 - X) = 1.0784 \text{ g}$

On solving, we get  $X = 0.518$

Percentage of NaCl = 57.36 %

Percentage of KCl = 42.64 %

24. The mineral haematite is  $\text{Fe}_2\text{O}_3$ . Haematite ore contain unwanted material called gangue in addition of  $\text{Fe}_2\text{O}_3$ . If 5.0 kg of ore contains 2.78 kg of Fe, what per cent of ore is  $\text{Fe}_2\text{O}_3$ ?



$$2 \times 55.85 \text{ g} \quad 159.7 \text{ g}$$

As  $2 \times 55.85 \text{ g}$  Fe is present in  $159.7 \text{ g}$   $\text{Fe}_2\text{O}_3$

So 2.78 kg Fe is present in

$$= \frac{159.7 \text{ g} \times 2.78 \text{ kg}}{2 \times 55.85 \text{ g}}$$

$$= 3.97 \text{ kg } \text{Fe}_2\text{O}_3$$

As 5 kg ore contains = 3.97 kg  $\text{Fe}_2\text{O}_3$

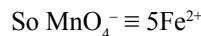
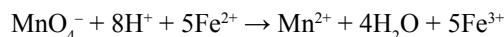
$$\text{So } 100 \text{ kg ore contains} = \frac{3.97 \times 100}{5}$$

$$= 79.4 \text{ kg } \text{Fe}_2\text{O}_3$$

Thus % of  $\text{Fe}_2\text{O}_3$  in ore = 79.4 %

25. 0.256 g sample of iron alloy (a mixture of iron with other elements) was dissolved in hydrochloric acid to give a solution of  $\text{Fe}^{2+}$  ion. This solution titrated to the end point with 35.6 ml of 0.1 N  $\text{KMnO}_4$ , which oxidized  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . What is the mass percentage of iron in the mixture?

**Solution** Reaction of  $\text{MnO}_4^-$  and  $\text{Fe}^{2+}$  in acidic medium is as follows:



$$\text{or } 5000 \text{ mL N } \text{KMnO}_4 = 5 \times 55.8 \text{ g of Fe}$$

$$35.6 \text{ mL of } 0.1 \text{ N } \text{KMnO}_4$$

$$= \frac{5 \times 55.8 \times 35.6 \times 0.1}{5000}$$

$$= 0.2 \text{ g Fe}$$

As 0.256 g alloy contains = 0.2 g Fe

$$\text{So } 100 \text{ g iron alloy contains} = \frac{0.2 \times 100}{0.256} \\ = 78.125 \%$$

## (ii) Problems Involving Mass–Volume or Weight–Volume Relationship

This relationship relates the mass of a reactant or product with the volume of another gaseous reactant or product involved in a chemical reaction.

For example,

Weight of a solid substance can be compared with the volume of gases with the help of the fact that 1 mole or 1 gram molecule of a gas occupies 22.4 litres or 22400 c.c. at N.T.P. So in brief, the weight-volume relationship can be represented as follows:



By mole	1	2	1	1
By amu	40	73	113	2
By gm.wt.	40 g	73 g	113 g	2g
By wt.	40 g	73 g	113 g	22.4
or vol.			lit at	
			NTP.	

For solving such problems one should proceed according to the following instructions given below:

- First, write down the relevant balanced chemical equation (s).
- Now write the weights of various solid reactants and products.
- Gases are normally expressed in terms of volumes. In case the volume of the gas is measured at the room temperature and pressure (that is, any condition other than NTP), convert it into N.T.P. by applying gas laws.
- The volume of a gas at any temperature and pressure can be converted into its weight and vice versa by using this relation,

$$PV = (g/M) \times RT$$

Here g is weight of gas, M is molecular weight of gas and R is gas constant.

- Finally, calculate the unknown factor (n or s) by unitary method.

### REMEMBER

One should not forget that if other conditions are not mentioned, the chemical reaction that is assumed to occur at N.T.P. that is, at 0°C (273 K) temperature and 760 mm (1 atmospheric) pressure.

## Illustrations

26. A mixture of aluminium and zinc weighing 1.67 grams was completely dissolved in acid and the evolved 1.69 litres of hydrogen gas measured at 273 K and one atmosphere pressure. What was the mass of aluminium in the original mixture?

**Solution** Let the mass of aluminium in the sample be 'A' g. The mass of Zn = (1.67 – A) g

$$\begin{aligned} \text{The volume of H}_2 \text{ at N.T.P. given by Al} \\ = \frac{3 \times 22.4 \times A}{2 \times 27} \text{ L} \end{aligned}$$

$$\text{The volume of H}_2 \text{ at NTP given by Zn}$$

$$= \frac{(1.67 - A) 22.4}{65.4} \text{ L}$$

$$\frac{3 \times 22.4 \times A}{54} + \frac{(1.67 - A) 22.4}{65.4} = 1.69$$

$$142.2 \times A = 176.26$$

$$A = 1.248 \text{ g}$$

27. In a titration experiment, 23.05 ml of 0.100 N NaOH was required to neutralize 10.00 ml of a solution of  $\text{H}_2\text{SO}_4$  of unknown strength. What was the normality of the acid solution?

**Solution** In a titration using NaOH and  $\text{H}_2\text{SO}_4$

$$\text{Meq of NaOH} = \text{Meq of H}_2\text{SO}_4$$

The meq. of NaOH used in the titration

$$\begin{aligned} 23.05 \text{ ml NaOH} \times 0.100 \frac{\text{meq of NaOH}}{\text{ml NaOH}} \\ = 2.31 \text{ meq. NaOH} \end{aligned}$$

The normality of the  $\text{H}_2\text{SO}_4$  solution

$$\begin{aligned} \frac{2.32 \text{ meq H}_2\text{SO}_4}{10.00 \text{ ml H}_2\text{SO}_4} = 0.231 \frac{\text{meq. H}_2\text{SO}_4}{\text{ml H}_2\text{SO}_4} \\ = 0.231 \text{ N H}_2\text{SO}_4 \end{aligned}$$

## 1.14 ■ Mole Concept and Stoichiometry

28. A 0.311 g sample of crude NaOH when dissolved in water required 46.1 ml of 0.122 N H<sub>2</sub>SO<sub>4</sub> to neutralize the NaOH in the sample. Calculate the per cent of NaOH in the sample.

**Solution** In a titration using NaOH and H<sub>2</sub>SO<sub>4</sub>

$$\text{Meq of NaOH} = \text{meq. of H}_2\text{SO}_4$$

The meq of H<sub>2</sub>SO<sub>4</sub>

$$0.122 \frac{\text{meq H}_2\text{SO}_4}{\text{ml solution}} \times 46.1 \text{ ml solution}$$

$$= 5.62 \text{ meq H}_2\text{SO}_4$$

The 5.62 meq. of NaOH

$$5.62 \text{ meq NaOH} \times 0.040 \frac{\text{g NaOH}}{\text{meq. NaOH}} \cdot \\ = 0.225 \text{ g NaOH}$$

The per cent of NaOH in the sample is as follows:

$$\frac{0.225 \text{ g NaOH}}{0.311 \text{ g sample}} \times 100 = 72.3 \% \text{ NaOH.}$$

29. A volume of 22.5 ml of 2.50 N NaOH was required to neutralize 10.5 ml of a solution of H<sub>2</sub>SO<sub>4</sub> of unknown strength. The density of the H<sub>2</sub>SO<sub>4</sub> solution was 1.16 g per ml. Calculate the per cent by weight of H<sub>2</sub>SO<sub>4</sub> in the solution.

**Solution** In a titration using NaOH and H<sub>2</sub>SO<sub>4</sub>

$$\text{Meq. of NaOH} = \text{meq. of H}_2\text{SO}_4$$

The meq. of NaOH:

$$2.50 \frac{\text{meq NaOH}}{\text{ml solution}} \times 22.5 \text{ ml solution}$$

$$= 56.3 \text{ meq NaOH}$$

The 56.3 meq. of H<sub>2</sub>SO<sub>4</sub>:

$$56.3 \text{ meq. H}_2\text{SO}_4 \times 0.0491 \frac{\text{g H}_2\text{SO}_4}{\text{meq. H}_2\text{SO}_4} \\ = 2.76 \text{ g H}_2\text{SO}_4$$

The weight of the 10.5 ml of H<sub>2</sub>SO<sub>4</sub>:

$$10.5 \text{ ml} \times 1.16 \frac{\text{g}}{\text{ml}} = 12.2 \text{ g}$$

The per cent H<sub>2</sub>SO<sub>4</sub> is

$$\frac{2.76 \text{ g H}_2\text{SO}_4}{12.2 \text{ g solution}} \times 100 \\ = 22.6 \% \text{ H}_2\text{SO}_4 \text{ by weight}$$

30. If required 33.6 ml of a 0.100 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution to oxidize the Fe<sup>2+</sup> to Fe<sup>3+</sup> in 21.6 ml of a solution of FeSO<sub>4</sub> of unknown strength.

**Solution** The equation is as follows:



1.00 mole                  6.00 moles

6.00 g-eq wt            6.00 g-eq wt



According to this equation, 1.00 g-eq wt of Fe<sup>2+</sup> ion will originate from 1.00 g-eq wt of FeSO<sub>4</sub>, we get meq. of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> = meq. of Fe<sup>2+</sup> = meq. of FeSO<sub>4</sub> meq. of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> is:

$$0.100 \frac{\text{meq Cr}_2\text{O}_7^{2-}}{\text{ml solution}} \times 33.6 \text{ ml solution} \\ = 3.36 \text{ meq. Cr}_2\text{O}_7^{2-}$$

The normality of the FeSO<sub>4</sub> solution is:

$$\frac{3.36 \text{ meq. FeSO}_4}{21.6 \text{ ml solution}} = 0.156 \text{ N FeSO}_4$$

As FeSO<sub>4</sub> solution is 0.156 N with respect to Fe<sup>2+</sup> ion, and the number of mg Fe<sup>2+</sup> per ml is as follows:

$$0.156 \frac{\text{meq Fe}^{2+}}{\text{ml solution}} \times 55.85 \frac{\text{mg Fe}^{2+}}{\text{meq. Fe}^{2+}} \cdot \\ = 8.71 \frac{\text{mg Fe}^{2+}}{\text{ml solution}} \cdot$$

31. What should be the weight of NaNO<sub>3</sub> to make 50 ml of an aqueous solution so that it contains 70 mg Na<sup>+</sup> ml<sup>-1</sup>?

**Solution** Molecular mass of NaNO<sub>3</sub> = 23 + 14 + 3 × 16

$$= 85 \text{ g mol}^{-1}$$

As 23 mg Na is present in 85 mg of NaNO<sub>3</sub>

$$\text{So 70 mg Na is present in } \frac{85 \times 70}{23}$$

$$= 258.7 \text{ mg NaNO}_3$$

As 1 ml solution contains 258.7 mg NaNO<sub>3</sub>,

So 50 ml solution contains

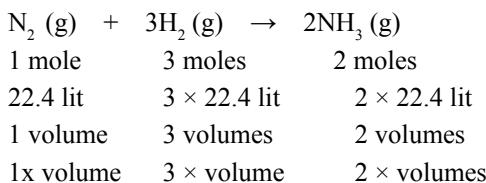
$$\begin{aligned} &= \frac{258.7 \text{ mg} \times 50 \text{ ml}}{1 \text{ ml}} \\ &= 13935 \text{ mg} \\ &= 13.935 \text{ g} \end{aligned}$$

### (iii) Problems Based on Volume–Volume Relationship

This relationship relates the volume of gaseous reactant or product with the volume of another gaseous reactant or product involved in a chemical reaction. For solving such problems, one should proceed according to the following instructions given below:

- First write down the relevant balanced chemical equation.
- Now write down the volume of reactants and products below the formula to each reactant and product using the fact that one gram molecule of every gaseous substance occupies 22.4 litres at N.T.P.
- If volume of the gas is measured under particular or room temperature, convert it to N.T.P. with the help of ideal gas equation.
- Now use Avogadro's hypothesis "gases under similar conditions of temperature and pressure contain the same number of molecules". Thus under similar conditions of temperature and pressure, the volume of reacting gases are proportional to the number of moles of the gases in the balanced equation.

Example,



From the above equation, it is clear that 22.4 litres of N<sub>2</sub> will react with 3×22.4 litres of H<sub>2</sub> to form 2×22.4 litres of NH<sub>3</sub>.

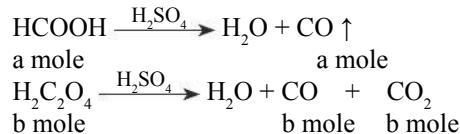
### Illustrations

32. A mixture of HCOOH and (COOH)<sub>2</sub> is heated with concentrated H<sub>2</sub>SO<sub>4</sub>. The gas produced is collected and on its treatment with KOH

solution the volume of the gas decreases by 1/6th. Calculate the molar ratio of two acids in the original mixture.

### Solution

#### Reactions



Total number of moles of CO and CO<sub>2</sub>

$$= a + b + b = a + 2b$$

Total number of moles of CO<sub>2</sub> = b

So Mole fraction of CO<sub>2</sub> absorbed in KOH

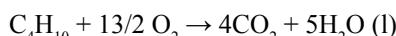
$$= \frac{b}{a + 2b}$$

$$\frac{b}{a + 2b} = \frac{1}{6}$$

$$a = 4b$$

Thus ratio of HCOOH and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is 4 : 1.

33. A gas mixture of 3 litre of propane (C<sub>3</sub>H<sub>8</sub>) and butane (C<sub>4</sub>H<sub>10</sub>) on complete combustion at 25°C produced 10 litre CO<sub>2</sub>. Find out the composition of gas mixture



Suppose x litre of C<sub>3</sub>H<sub>8</sub> and y litre of C<sub>4</sub>H<sub>10</sub> are present in the mixture.

$$\text{So } x + y = 3 \quad \dots\dots\dots(1)$$

As volume of CO<sub>2</sub> formed = 10 = CO<sub>2</sub> formed by C<sub>3</sub>H<sub>8</sub> + CO<sub>2</sub> formed by C<sub>4</sub>H<sub>10</sub>

$$10 = 3x + 4y \quad \dots\dots\dots(2)$$

Solving Eqs. 1. and 2.

$$y = 1 \text{ litre}$$

$$x = 2 \text{ litre}$$

### n-Factor or Valence Factor

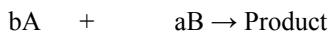
It is very important for both redox reactions and non-redox reactions by which we can obtain following informations:

## 1.16 ■ Mole Concept and Stoichiometry

(i) It calculates the molar ratio of the species taking part in reactions that is, reactants. The reciprocal of n-factor's ratio of the reactants represents the molar ratio of the reactants.

Example, If A (having n-factor = a) reacts with B (having n-factor = b) then its n-factor's ratio is a : b, so molar ratio of A to B is b : a.

It can be represented as follows:



(n-factor = a) (n-factor = b)

$$(ii) \text{ Equivalent weight} = \frac{\text{Molecular weight}}{\text{n-factor}}$$

or

$$\frac{\text{Atomic weight}}{\text{n-factor}}$$

### Calculation of n-Factor

Before calculating the n-factor of any of the reactant in a given chemical reaction we must have a clear idea about the type of reaction. The reaction may be any of these types:

- (i) Acid base or neutralization reaction
- (ii) Redox reaction
- (iii) Precipitation or double decomposition reaction

#### **(i) Acid–Base or Neutralization Reactions:**

As we know that according to the Arrhenius concept, “An acid provides H<sup>+</sup> ion(s) while a base provides OH<sup>-</sup> ion(s) in neutralization these H<sup>+</sup> and OH<sup>-</sup> ion/ions combines together”.

The number of H<sup>+</sup> ion(s) and OH<sup>-</sup> ion(s) represent n-factor for acid and base respectively, that is, basicity and acidity respectively.

Example,



(n = 1) that is, monobasic acid



(n = 2) that is, dibasic acid



(n = 3) that is, tribasic acid



(n = 1) that is, monoacidic base



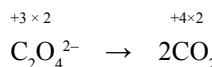
(n = 2) that is, diacidic base



(n = 3) that is, triacidic base

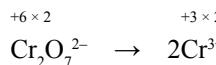
**(ii) Redox Reactions:** These reactions involve oxidation and reduction simultaneously. Here exchange of electrons occurs. To find n-factor for oxidizing or reducing agent we must find out the change in oxidation state of these species.

Example (1) When only one atom undergoes oxidation or reduction



n = 2

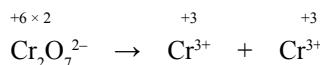
$$\text{n-factor} = |(+4) \times 2 - (+3) \times 2| = 2$$



n = 6

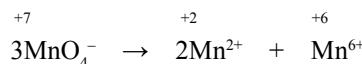
$$\text{n-factor} = |(+3) \times 2 - (+6) \times 2| = 6$$

Example (2) For the salt which react in such a way that one atom undergoes change in oxidation state but appear in two product having same oxidation state.



$$\text{n-factor} = |(+6) \times 2 - (+3) \times 2| = 6$$

Example (3) For the salts which react in such a way that one atom undergoes change in oxidation state but appear in two product having different oxidation state.



$$= |2 \times (+2) - 2 \times (+7)| + |1 \times (+6) - 1 \times (+7)| = |4 - 14| + |6 - 7| = 11$$

Hence n-factor = 11/3.

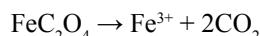
Example (4) For the salts which react in such a way that one atom undergoes change in oxidation state in

two products one with changed oxidation state from that of reactant and another having same oxidation state as that of reactant.



Here, out of 14 moles of  $\text{Cl}^-$  (in HCl) only 6 moles of  $\text{Cl}^-$  are changing the oxidation state from  $-1$  to  $0$  in the product  $\text{Cl}_2$  while the oxidation state of remaining 8  $\text{Cl}^-$  ions remains the same in HCl and  $\text{CrCl}_3$ . Hence the total number of moles of electrons lost by 14 moles of HCl is 6 here. So each mole of HCl takes up  $6/14$  that is,  $3/7$  moles of electrons and hence n-factor of HCl is  $3/7$ .

**Example (5)** For the salt which react in such a way that two or more atoms undergoes change in oxidation states.

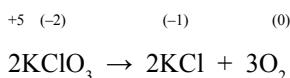


Here, the oxidation state of Fe in this form  $+2$  to  $+3$  while that of C change from  $+3$  to  $+4$ . Here n-factor can be find out by calculating the total change in oxidation state per mole of the salt. Here 1 mole of  $\text{FeC}_2\text{O}_4$  have one of  $\text{Fe}^{2+}$  and one mole of  $\text{C}_2\text{O}_4^{2-}$  so the total change in oxidation state is given as

$$\begin{aligned} &= |1 \times (+2) - 1 \times (+3)| + |2 \times (+3) - 2 \times (+4)| \\ &= 1 + 2 = 3 \end{aligned}$$

Hence n-factor of  $\text{FeC}_2\text{O}_4$  is 3.

**Example (6)** Salts or compounds which undergo intramolecular redox reaction that is, in which an atom undergoes oxidation while another atom undergoes reduction. Here n-factor can be find out by knowing the balanced chemical reaction and considering only one process.



In this reaction, oxidation atom is getting oxidized while chlorine atom is getting reduced so

n-factor of  $\text{KClO}_3$  considering oxidation

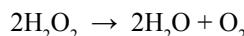
$$= |3 \times (-2) - 3 \times (0)| = 6$$

n-factor of  $\text{KClO}_3$  considering reduction

$$= |1 \times 5 - 1 \times (-1)| = 6$$

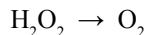
**Example (7)** Salts or compounds which undergo disproportion reaction that is, in which a single species

undergoes oxidation as well as reduction. Here, n-factor can be found out by knowing the balanced chemical reaction and considering only one process.



Here out of these two  $\text{H}_2\text{O}_2$  molecules shown by the reaction one mole of  $\text{H}_2\text{O}_2$  is oxidized and one mole is reduced.

For oxidation reaction



$$\text{n-factor} = |2 \times 0 - (-1) \times 2| = 2$$

For reduction reaction



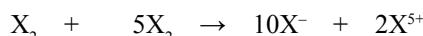
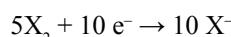
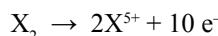
$$\text{n-factor} = |(-2) \times 2 - (-1) \times 2| = 2$$

Hence n-factor of  $\text{H}_2\text{O}_2$  in both oxidation and reduction reaction is same that is, 2.

In the disproportion reactions in which moles of compounds undergoing oxidation and reduction are not same like.



Here out of 6 moles of  $\text{X}_2$ , 5 moles of  $\text{X}_2$  undergo reduction and accept 10 moles of electrons (oxidizing agent) while 1 mole of  $\text{X}_2$  undergoes oxidation by loosing 10 moles of electrons (reducing agents)



$$(n=10) \quad (n=2) \quad (n=1) \quad (n=5)$$

Reducing Oxidizing

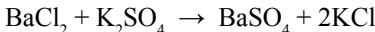
agent agent

Hence n-factor of  $\text{X}_2$  acting as oxidizing agent is 2 and that  $\text{X}_2$  acting as reducing agent has n-factor 10.

### (iii) Precipitation or Double decomposition Reaction:

It is the reaction in which there is no change in oxidation state for any atom. Here n-factor of the salt used in the reaction can be found out by multiplying the oxidation state of the cation or anion by the total number of atoms per molecule of the salt.

## 1.18 ■ Mole Concept and Stoichiometry



$$(n = 2) \quad (n = 2)$$

For  $\text{BaCl}_2$

n-factor = Oxidation state of Ba atom in  $\text{BaCl}_2$  × number of Ba atoms in one molecule of  $\text{BaCl}_2$

$$= (+2) \times 1 = 2$$

For  $\text{K}_2\text{SO}_4$

n-factor = Oxidation state of K × number of K-atoms in one molecule of  $\text{K}_2\text{SO}_4$

$$= (+1) \times 2 = 2$$

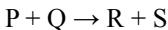
### Laws of Equivalence

According to law of equivalence, for each and every reactant and product,

Equivalents of each reactant reacted = Equivalents of each product formed.

Example,

Suppose the reaction is taking place as follows:



According to law of equivalence,

Equivalents of P reacted

= Equivalents of Q reacted

= Equivalents of R produced

= Equivalents of S produced

Equivalents of any substance

$$= \frac{\text{Weight of substance (in g)}}{\text{Equivalent weight}}$$

$$= \text{Normality (N)} \times \text{Volume (V)} \text{ (In litre)}$$

$$\text{Normality (N)} = \text{n-Factor} \times \text{Molarity (M)}$$

Normality and molarity are temperature dependent. As on changing the temperature, the volume of solution changes, so normality and molarity change.

### POAC (Principle of Atom Conservation) Method

For any chemical reaction, mole atom of any element remain conserved during the chemical reaction.

### Illustrations

34.  $2.68 \times 10^{-3}$  moles of a solution containing an ion  $\text{A}^{\text{n}+}$  required  $1.61 \times 10^{-3}$  moles of  $\text{MnO}_4^-$  for the oxidation of  $\text{A}^{\text{n}+}$  to  $\text{AO}_3^-$  in an acidic medium. What is the value of n?

**Solution** As  $1.61 \times 10^{-3}$  M  $\text{KMnO}_4$   $\equiv 2.68 \times 10^{-3}$  M solution of  $\text{A}^{\text{n}+}$

$$\text{So M/5 KMnO}_4 = \frac{2.68 \times 10^{-3} \text{ M}}{1.61 \times 10^{-3}} \times \frac{\text{M}}{5}$$
$$= 0.33 \text{ M solution of A}^{\text{n}+}$$

$$0.33 \text{ M} = \frac{\text{M}}{5 - n}.$$

$$5 - n = \frac{1}{0.33} = 3$$

$$n = 2$$

35. One g of impure  $\text{Na}_2\text{CO}_3$  is dissolved in water and the solution is made upto 250 ml. To 50 ml of this made up solution, 50 ml of 0.1 N HCl is added and the mixture after shaking well required 10 ml of 0.16 N sodium hydroxide solution for complete neutralization. Calculate the per cent purity of the sample of  $\text{Na}_2\text{CO}_3$ .

**Solution** Strength of the  $\text{Na}_2\text{CO}_3$  solution = 4 g L<sup>-1</sup>

Suppose the normality of  $\text{Na}_2\text{CO}_3$  solution = Nx

As after mixing  $\text{Na}_2\text{CO}_3$  and HCl solution, NaOH solution is added so according to normality equation

$$50 \times Nx + 0.16 \times 10 = 50 \times 0.1$$

$$Nx = 0.068 \text{ N}$$

$$\text{Strength (g L}^{-1}\text{)} = \text{Normality} \times \text{Equivalent mass}$$

$$= 0.068 \times 53 = 3.6 \text{ g L}^{-1}$$

$$\text{So purity of Na}_2\text{CO}_3 = \frac{3.6 \times 100}{4}$$
$$= 90 \text{ %}.$$

36. 0.257 g of a nitrogenous compound was digested with sulphuric acid and then distilled with excess of strong alkali. The gas evolved was absorbed in 50 ml N/10  $\text{H}_2\text{SO}_4$ . At the end of the experiment, the acid required 20.2 ml of

N/10 NaOH for neutralization. Determine the percentage of nitrogen in the substance.

**Solution** 23.2 ml of N/10 NaOH  $\equiv$  23.2 ml of N/10



Volume of N/10 H<sub>2</sub>SO<sub>4</sub> neutralized by NH<sub>3</sub>

$$= 50 - 23.2 = 26.8 \text{ ml}$$

26.8 ml of N/10 H<sub>2</sub>SO<sub>4</sub>  $\equiv$  26.8 ml of N/10 NH<sub>3</sub>

$\equiv$  26.8 ml of N/10 nitrogen

26.8 ml of N/10 nitrogen will contain

$$\frac{14}{1000} \times \frac{26.8}{1000} \text{ g nitrogen}$$

The mass of nitrogen was originally present in 0.257 g of the organic substance.

So % of nitrogen

$$= \frac{14}{10} \times \frac{26.8}{1000} \times \frac{100}{0.257} = 14.6 \%$$

## Volumetric Analysis (Titration)

Volumetric analysis is an analytical method used to find the concentration of a substance in a solution by adding exactly same number equivalents of some another substance present in a solution of known concentration (standard solution).

Volumetric analysis is also called titrimetric analysis. Here the substance whose solution is used to find the concentration of unknown solution is known as titrant and the substance whose concentration is to be calculated is known as titrate.

## Types of Titration

Titration or volumetric analysis is of following types:

1. Simple titration
2. Double titration
3. Back titration
4. Iodimetric and iodometric titration

## Simple Titration

The purpose of this titration is to find the concentration of an unknown solution by using the known concentration of another solution. Here a known volume

the solution of unknown concentration is taken in a flask and the essential reagents are ended in it. Now the solution of known concentration is added from the burette in this solution till complete reaction occurs between them and the end point or equivalence point of the two reacting species are equal.

For example,

If we take two solution X and Y then at the end point

$$N_x V_x = N_y V_y$$

Here N<sub>x</sub> = Normality of solution X

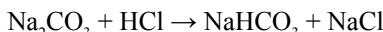
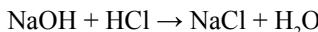
V<sub>X</sub> = Volume of solution X

N<sub>y</sub> = Normality of solution Y

V<sub>y</sub> = Volume of solution Y

## Double Titration

This titration is used for specific compounds using various indicators. When the solution having NaOH and Na<sub>2</sub>CO<sub>3</sub> is titrated using phenolphthalein indicator, at phenolphthalein end point following reactions take place:



Here Equivalents of NaOH +  $\frac{1}{2}$  equivalents of Na<sub>2</sub>CO<sub>3</sub> = Equivalents of HCl ..... (i)

When methyl orange is used, Na<sub>2</sub>CO<sub>3</sub> is converted into NaCl + CO<sub>2</sub> + H<sub>2</sub>O

Equivalents of NaOH + Equivalents of Na<sub>2</sub>CO<sub>3</sub> = Equivalents of HCl ..... (ii)

These titrations are carried out by using phenolphthalein and methyl orange in continuation as well as separately also.

We apply law of equivalents to find the percentage composition of the mixture with the help of equation (i) and (ii) if the HCl consumption in two different steps is given.

■ Phenolphthalein indicates end point when Na<sub>2</sub>CO<sub>3</sub> is converted into NaHCO<sub>3</sub>.

## Back Titration

Suppose we have an impure solid substance 'O' weighing 'w' gm and we have to find the percentage purity of 'O' in the given sample. We have also

## 1.20 ■ Mole Concept and Stoichiometry

been given two solutions ‘M’, ‘N’ here the concentration of ‘N’ is known ‘N<sub>1</sub>’ and that of ‘M’ is unknown. For a back titration to be carried out; the following conditions must be satisfied.

- (i) Compounds ‘M’, ‘N’ and ‘O’ must be such that ‘M’ and ‘N’ can react with each other.
- (ii) ‘M’ and pure ‘O’ can also react with each other however the impurities present in ‘O’ must not react with ‘M’.
- (iii) The product of ‘M’ and ‘O’ should not react with ‘N’.

Now we will take a certain volume of ‘M’ in a flask but remember the equivalents of ‘M’ taken must be greater or equal to equivalents of pure ‘O’ in the sample and perform a simple titration using ‘N’. Here we assume that the volume of ‘N’ used is ‘V<sub>1</sub>’ litre.

$$\text{Equivalents of 'N' reacted with 'M'} = N_1 V_1$$

$$\text{Hence initial equivalents of 'M'} = N_1 V_1$$

Now we will take same volume of ‘M’ in another flask however now ‘O’ is added in the flask. Here pure part of ‘O’ reacts with ‘M’ and excess of ‘M’ is back titrated with ‘N’. Suppose the volume of ‘N’ consumed is V<sub>2</sub> litre here.

Equivalents of ‘N’ reacted with excess of ‘M’

$$= N_1 V_2$$

Hence equivalent of ‘M’ in excess = N<sub>1</sub> V<sub>2</sub>  
that is, equivalent of ‘M’ reacted pure ‘O’

$$= (N_1 V_1 - N_1 V_2)$$

$$\text{Equivalents of pure 'O'} = (N_1 V_1 - N_1 V_2)$$

Suppose the n-factor of ‘O’ in its reaction with ‘M’ is ‘a’ then the moles of pure ‘O’

$$= \frac{(N_1 V_1 - N_1 V_2)}{a}$$

Hence mass of pure ‘O’

$$= \frac{(N_1 V_1 - N_1 V_2)}{a} \times \text{Molar mass of 'O'}$$

Percentage purity of ‘O’

$$= \frac{(N_1 V_1 - N_1 V_2)}{a} \times \frac{\text{Molar mass of 'O'}}{w} \times 100$$

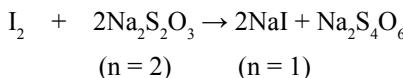
## Iodimetric and Iodometric Titrations

When in redox titrations iodine is used as an oxidizing agent these titrations are called iodine titration. These are of two types:

### Iodimetic Titration

In such titrations iodine solution is used as an oxidant and iodine is directly titrated against a reducing agent. This type of titrations are used for the determination of strength of reducing agents like sulphides, arsenides, thiosulphates etc., by titrating them against a standard solution of iodine.

This type of titration involves free iodine. Here iodine solution is treated with known sodium thiosulphate solution having a normality, N and volume V litre.



$$\begin{aligned} \text{Equivalents of I}_2 &= \text{Equivalents of Na}_2\text{S}_2\text{O}_3 \text{ used} \\ &= N \times V \end{aligned}$$

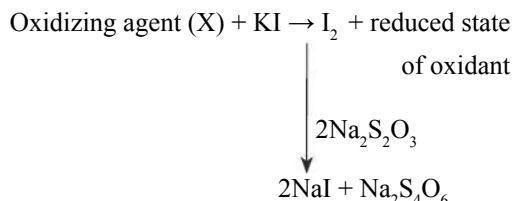
$$\text{Moles of I}_2 = \frac{N \times V}{2}$$

$$\text{Mass of free I}_2 \text{ in the solution} = \left( \frac{N \times V}{2} \times 254 \right) \text{ g}$$

### Iodometric Titration

It is an indirect method of estimation of iodine. In this titration an oxidizing agent is used to liberate iodine from iodine solution and the liberated iodine is treated with a standard solution of a reducing agent added from a burette. Here a neutral or an acidic solution of an oxidizing agent is used and the amount of liberated I<sub>2</sub> is equal to the quantity of this oxidizing agent.

These titrations are used to determine the concentration of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, KMnO<sub>4</sub>, CuSO<sub>4</sub>, Ferric ions, H<sub>2</sub>O<sub>2</sub> etc.



Equivalents of (X) = Equivalents of  $I_2$  = Equivalents of  $Na_2S_2O_3$  used =  $N \times V$

Equivalents of  $I_2$  liberated from KI =  $N \times V$

Equivalents of (X) =  $N \times V$

Let the n-factor of (X) in its reaction with KI be x, then

$$\text{Mass of (X) consumed} = \frac{N \times V}{x} \times MX$$

(Here  $M_x$  is the molar mass of (X)).

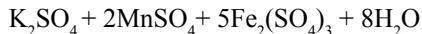
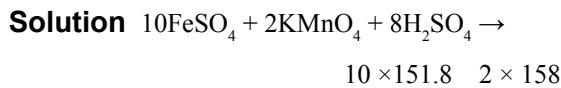
### REMEMBER



(complex soluble in water and provide  $K^+$  and  $I_3^-$ )

### Illustrations

37. How many mL of a 0.05 M  $KMnO_4$  solution are required to oxidize 2.0 g of  $FeSO_4$  in a dilute solution (acidic)?



10 × 151.8 g of  $FeSO_4$  require  $KMnO_4 = 2 \times 158$  g

2 g of  $FeSO_4$  will require  $KMnO_4 = \frac{2 \times 158 \times 2}{10 \times 151.8}$

Suppose V ml of  $KMnO_4$  solution (0.05 M) is required.

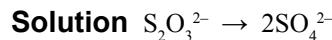
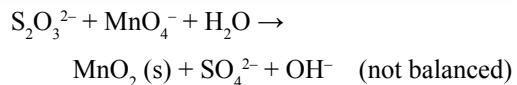
Amount of  $KMnO_4$  in this solution

$$= \frac{158 \times 0.05}{1000} \times V$$

$$\text{Thus, } \frac{158 \times 0.05 \times V}{1000} = \frac{2 \times 158 \times 2}{10 \times 151.8}$$

$$V = 52.7 \text{ ml}$$

38. 0.1 M  $KMnO_4$  is used for the following titration. What volume of the solution in mL will be required to react with 0.158 g of  $Na_2S_2O_3$ ?



Change in oxidation number of sulphur per molecule of  $S_2O_3^{2-}$

$$= 2 \times (6 - 2) = 8$$

Change in oxidation number of Mn per molecule of  $MnO_4^-$

$$= 7 - 4 = 3$$

$$\text{No. of moles in 0.158 g of } Na_2S_2O_3 \\ = \frac{0.158}{158} = 1 \times 10^{-3}$$

$$\text{No. of equivalents} = 8 \times 10^{-3}$$

Normality of 0.1 M  $KMnO_4$  solution

$$= 0.1 \times 3 = 0.3$$

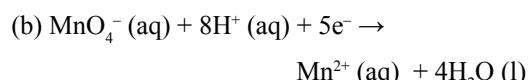
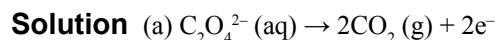
Suppose V ml of  $KMnO_4$  is required then

$$\frac{V}{1000} \times 0.3 = 8 \times 10^{-3}$$

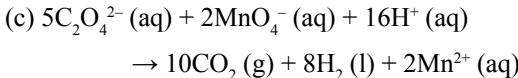
$$\text{So } V = \frac{8}{0.3} \times 10^{-3} \times 10^3 \\ = 26.7 \text{ ml}$$

39. (a) Give a half-equation for the oxidation of the ethanedioate ion,  $C_2O_4^{2-}$  (aq), to carbon dioxide  $CO_2$  (g).
- (b) Give a half equation for the reduction of the manganate (VII) ion,  $MnO_4^-$  (aq), to manganese (II) ions,  $Mn^{2+}$  (aq), in acidic conditions.
- (c) Calculate the volume of an acidified solution of 0.02 M potassium manganate (VII),  $KMnO_4$ , which would be needed to oxidize 100 cm<sup>3</sup> of a saturated solution of magnesium ethanedioate,  $MgC_2O_4$ .

Solubility of magnesium ethanedioate at 20°C is  $9.3 \times 10^{-3}$  mol dm<sup>-3</sup>.



## 1.22 ■ Mole Concept and Stoichiometry



100 cm<sup>3</sup> of saturated MgC<sub>2</sub>O<sub>4</sub> solution at 20°C contains  $9.3 \times 10^{-4}$  mol.

According to the equation,

As 5 mol of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> react with 2 mol MnO<sub>4</sub><sup>-</sup>.

So  $9.3 \times 10^{-4}$  mol of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> react with

$$\frac{2 \times 9.3 \times 10^{-4}}{5} \text{ mol}$$

As 1000 cm<sup>3</sup> of 0.02 M MnO<sub>4</sub><sup>-</sup> contains 0.02 mol MnO<sub>4</sub><sup>-</sup>.

$$\text{So } \frac{1000 \times 2 \times 9.3 \times 10^{-4}}{0.02 \times 5} \text{ cm}^3$$

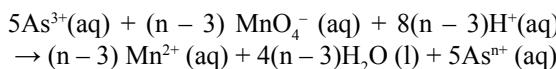
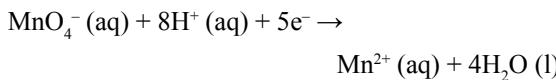
of 0.02 M MnO<sub>4</sub><sup>-</sup>

$$\text{contains } \frac{2 \times 9.3 \times 10^{-4}}{5} \text{ mol}$$

$$= 18.6 \text{ cm}^3$$

40. A solution of arsenic (III) oxide containing 0.248 g required 50 cm<sup>3</sup> of acidified potassium permanganate (VII) solution (0.02 mol dm<sup>-3</sup>) for complete oxidation. What is the oxidation state of arsenic in the product? [A<sub>r</sub>(O) = 16, A<sub>r</sub>(As) = 75]

**Solution** As<sup>3+</sup>(aq) → As<sup>n+</sup>(aq) + (n - 3)e<sup>-</sup>



$$\begin{aligned} \text{Number of moles As}_2\text{O}_3 &= \frac{0.248}{150 + 48} \\ &= 0.00125 \text{ moles} \end{aligned}$$

Number of moles As<sup>3+</sup> = 0.0025 moles

50 cm<sup>3</sup> of potassium permanganate (VII) (0.02 mol dm<sup>-3</sup>) contains

$$\frac{50 \times 0.02}{1000} \text{ moles}$$

= 0.001 moles potassium permanganate (VII)

As 0.0025 moles As<sup>3+</sup> reacts with 0.001 mole MnO<sub>4</sub><sup>-</sup>

So 2.5 mole As<sup>3+</sup> reacts with 1 mole MnO<sub>4</sub><sup>-</sup>

In this equation,

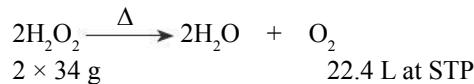
$$\text{Ratio } \frac{2.5}{1} = \frac{5}{\text{n} - 3} .$$

Oxidation state of arsenic in the product = +5.

### Volume Strength of H<sub>2</sub>O<sub>2</sub> Solution

The concentration of H<sub>2</sub>O<sub>2</sub> is usually represented in terms of volume. If a sample of H<sub>2</sub>O<sub>2</sub> is labelled as 'X' volume, it means that 1 volume of H<sub>2</sub>O<sub>2</sub> solution gives 'X' volumes of O<sub>2</sub> gas at STP on complete decomposition.

Consider the decomposition of H<sub>2</sub>O<sub>2</sub> as



As 22400 ml of O<sub>2</sub> gas is liberated by 68 g of H<sub>2</sub>O<sub>2</sub> solution

So X ml of O<sub>2</sub> gas will be liberated by

$$= \frac{68 \text{ X}}{22400} = \frac{17 \text{ X}}{5600} \text{ g of H}_2\text{O}_2$$

It means that  $17\text{X}/5600$  g of H<sub>2</sub>O<sub>2</sub> will be present in 1 ml of solution.

1000 ml of solution contains H<sub>2</sub>O<sub>2</sub>

$$= \frac{17\text{X}}{5600} \times 1000 = \frac{17 \text{ X}}{5.6}$$

Strength (g L<sup>-1</sup>) = Normality × Equivalent wt.

$$\frac{17\text{X}}{5.6} = \text{N} \times \frac{34}{2} \text{ (n-factor of H}_2\text{O}_2 = 2)$$

$$\text{X} = 5.6 \times \text{N}$$

that is, **Volume strength of H<sub>2</sub>O<sub>2</sub> = 5.6 × Normality**

### Illustrations

41. The label on a H<sub>2</sub>O<sub>2</sub> bottle reads as 10 Vol. Find the concentration of the H<sub>2</sub>O<sub>2</sub>%.

**Solution** 2H<sub>2</sub>O<sub>2</sub> → 2H<sub>2</sub>O + O<sub>2</sub>

10 vol. means 1 vol H<sub>2</sub>O<sub>2</sub> = 10 ml O<sub>2</sub>

$$1 \text{ g H}_2\text{O}_2 = \frac{22400}{68} = 329 \text{ ml}$$

1 litre of 10 vol. means = 10000 ml of O<sub>2</sub>

Weight of  $\text{H}_2\text{O}_2$  to give 10000 ml

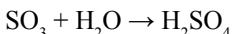
$$= \frac{1}{329} \times 10000 = 30.4 \text{ g}$$

Conc. = 30.4 g/lit

$$\text{Conc. \%} = 30.4 \times \frac{100}{1000} = 3.04 \text{ \%}$$

## Percentage Labelling of Oleum

Oleum or fuming sulphuric acid contains  $\text{SO}_3$  gas dissolved in sulphuric acid. When water is added to oleum,  $\text{SO}_3$  reacts with  $\text{H}_2\text{O}$  to form  $\text{H}_2\text{SO}_4$  as a result mass of the solution increases.

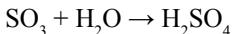


The total mass of  $\text{H}_2\text{SO}_4$  obtained by diluting 100 g of sample of oleum with desired amount of water, is equal to the percentage labelling of oleum.

% labelling of oleum = Total mass of  $\text{H}_2\text{SO}_4$  present in oleum after dilution.

= mass of  $\text{H}_2\text{SO}_4$  initially present + mass of  $\text{H}_2\text{SO}_4$  produced on dilution.

Suppose the mass of oleum sample be 100 g, which on dilution becomes 109 g. This implies that 9 g of  $\text{H}_2\text{O}$  was added.



Moles of  $\text{H}_2\text{O}$  added =  $9/18$  = Moles of  $\text{SO}_3$  present in oleum sample.

$$\text{Mass of } \text{SO}_3 \text{ in oleum} = \frac{9}{18} \times 80 = 40 \text{ g}$$

Thus, oleum sample contained 40 %  $\text{SO}_3$  and 60 %  $\text{H}_2\text{SO}_4$ .

## Illustrations

42. Find the percentage of free  $\text{SO}_3$  in an Oleum sample which is labelled 112 %  $\text{H}_2\text{SO}_4$ .

**Solution** Oleum =  $\text{H}_2\text{SO}_4 + \text{SO}_3 = \text{H}_2\text{S}_7\text{O}_7$

If initial weight of labelled  $\text{H}_2\text{S}_7\text{O}_7$  = 100 gm

Weight of  $\text{H}_2\text{SO}_4$ , after dilution = 112

Wt. of  $\text{H}_2\text{O}$  = 12 gm

$$\text{Moles of } \text{H}_2\text{O} = \text{moles of } \text{SO}_3 = \frac{12}{18} = 0.66$$

$$\text{Wt. of } \text{SO}_3 = 0.66 \times 80 = 52.8$$

$$\% \text{ of } \text{SO}_3 = \frac{\text{Wt. of } \text{SO}_3 \times 100}{100}$$

$$= 52.8 \%$$

## Hardness of Water

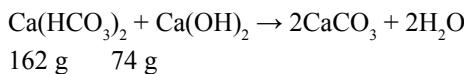
The hardness of water is due to the presence of bicarbonates, chlorides and sulphates of calcium and magnesium. Bicarbonates causes temporary hardness while chlorides and sulphates causes permanent hardness. The extent of hardness is called degree of hardness. It is defined as the number of parts by weight of calcium carbonate present in one million parts by weight of water that is, in ppm (milligram per litre) of  $\text{CaCO}_3$ .

$$\text{Hardness of water} = \frac{\text{gm of calcium carbonate}}{10^6 \text{ gm of water}}$$

## Illustrations

43. 50 litres of water containing  $\text{Ca}(\text{HCO}_3)_2$  when converted into soft water required 22.2 g  $\text{Ca}(\text{OH})_2$ . Calculate the amount of  $\text{Ca}(\text{HCO}_3)_2$  per litre of hard water.

**Solution** Reaction



As 74 g  $\text{Ca}(\text{OH})_2$  reacts with 162 g  $\text{Ca}(\text{HCO}_3)_2$

So 22.2 g  $\text{Ca}(\text{OH})_2$  will react with

$$= \frac{162 \times 22.2}{74}$$

$$= 48.6 \text{ g } \text{Ca}(\text{HCO}_3)_2$$

As 50 L water contains = 48.6 g  $\text{Ca}(\text{HCO}_3)_2$

$$\text{So 1 L water contains} = \frac{48.6}{50}$$

$$= 0.972 \text{ g L}^{-1}$$

44. One litre of a sample of hard water contains 0.9 mg of  $\text{CaCl}_2$  and 0.9 mg of  $\text{MgCl}_2$ . Find the total hardness in terms of parts of  $\text{CaCO}_3$  per  $10^6$  parts of water by mass.

## 1.24 ■ Mole Concept and Stoichiometry

**Solution** Mol. mass of  $\text{CaCl}_2$  = 111

Mol. mass of  $\text{MgCl}_2$  = 95

111 g of  $\text{CaCl}_2$   $\equiv$  100 g of  $\text{CaCO}_3$

0.9 mg of  $\text{CaCl}_2$   $\equiv$   $\frac{100}{111} \times 0.9$  mg of  $\text{CaCO}_3$

= 0.81 mg of  $\text{CaCO}_3$

95 g of  $\text{MgCl}_2$   $\equiv$  100 g of  $\text{CaCO}_3$

0.9 g of  $\text{MgCl}_2$   $\equiv$   $\frac{100}{95} \times 0.9$  of  $\text{CaCO}_3$

= 0.94 mg of  $\text{CaCO}_3$

Thus, one litre of hard water contains  $(0.81 + 0.94)$

= 1.75 mg of  $\text{CaCO}_3$

One litre of water  $10^3$  g =  $10^6$  mg

Degree of hardness = 1.75 ppm

### Enhance Your Knowledge

■ 1 mole of  $\text{H}_2\text{O} \neq 22400$  ml or cc. of  $\text{H}_2\text{O}$   
(since it is liquid)

1 mol of  $\text{H}_2\text{O} = 18$  cc. of  $\text{H}_2\text{O}$   
(as density of  $\text{H}_2\text{O} = 1\text{gm/cc}$ )

■ Mass of one mole of  $e^-$  = mass of one  $e^- \times N_A$   
 $= 9.1 \times 10^{-31} \times 6.02 \times 10^{23}$   
 $= 0.55$  mg.

■ Some substances like  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  have a tendency to lose water in air. These are called efflorescent and this tendency is called efflorescence.

■ Some solid substances like  $\text{NaOH}$ ,  $\text{KOH}$ , which have a tendency to absorb moisture greatly from air and to get wet are called 'Deliquescent' and this tendency is called Deliquescence.

■ Hygroscopic substances like quicklime ( $\text{CaO}$ ), anhydrous  $\text{P}_2\text{O}_5$  etc., absorb moisture from air.

■ To find equivalent weight of an acid:

It is possible by Silver Salt Formation Method.

$$\frac{\text{Eq. wt. of R-COOAg}}{108} = \frac{\text{Wt. of R-COOAg}}{\text{wt. of Ag}}$$

■ Eq. wt. of R-COOH  
= Eq. wt. of R-COOAg - 107

### In Redox Titration

$$V(\text{oxidizing agent}) \times M(\text{oxidizing agent}) =$$

$$V(\text{reducing agent}) \times M(\text{reducing agent})$$

$$\times \frac{\text{No. of moles of oxidizing agent}}{\text{No. of moles of reducing agent}}$$

### In Acid Base Titration

$$V(\text{acid}) \times M(\text{acid}) =$$

$$V(\text{base}) \times (M \text{ base}) \times \frac{\text{No. of moles of acid}}{\text{No. of moles of base}}$$

$$Z_1 M_1 V_1 = Z_2 M_2 V_2$$

Here  $Z_1$  = acidity or basicity of substance - 1

and  $Z_2$  = acidity or basicity of substance - 2

For a mixture of solution of non reacting substances.

$$N_1 V_1 + N_2 V_2 + N_3 V_3 = N_{\text{mix.}} V_{\text{mix.}}$$

If all the three acids are monobasic or bases are monoacidic,

$$M_1 V_1 + M_2 V_2 + M_3 V_3 = M_{\text{mix.}} V_{\text{mix.}}$$

If we mix HCl and  $\text{H}_2\text{SO}_4$  then, 'M' of  $\text{H}_2\text{SO}_4$  will be multiplied by 2 because  $\text{H}_2\text{SO}_4$  is dibasic acid.

**Law of equivalence is used only in following conditions**

If either a substance or solution reacts completely with a known volume of a standard solution, then

Number of equivalents of substance = Number of equivalents of standard solution.

$$\frac{W_{\text{Sub}}}{\text{Eq. wt.}_{\text{Sub}}} = \frac{NV}{1000} .$$

$$N_1 V_1 = N_2 V_2$$

Number of eq. of metal = Number of eq. of solution

$$\frac{W}{\text{Eq. wt.}} = \frac{NV}{1000} \text{ solution.}$$

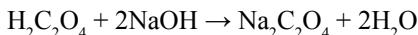
## Solved Problems from the IITs

1. A mixture of  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{NaHC}_2\text{O}_4$  weighing 2.02 g was dissolved in water and the solution made up to one litre. 10 ml of this solution required 3.0 ml of 0.1 N NaOH solution for complete neutralization. In another experiment 10 ml of same solution in hot dilute  $\text{H}_2\text{SO}_4$  medium required 4 ml of 0.1 N  $\text{KMnO}_4$  for complete neutralization. Calculate the amount of  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{NaHC}_2\text{O}_4$  in the mixture.

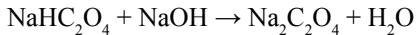
[IIT 1990]

**Solution** Suppose mass of  $\text{H}_2\text{C}_2\text{O}_4$  present in the mixture is 'X' g in 1 litre and mass of  $\text{NaHC}_2\text{O}_4$  present in the mixture is 'Y' g in 1 litre.

### For acid-base reaction



$$\begin{aligned}\text{Equivalent mass of } \text{H}_2\text{C}_2\text{O}_4 &= \frac{\text{Mol. mass}}{2} \\ &= \frac{90}{2} = 45\end{aligned}$$



$$\begin{aligned}\text{Equivalent mass of } \text{NaHC}_2\text{O}_4 &= \frac{\text{Mol. mass}}{1} \\ &= 112\end{aligned}$$

Equivalent of  $\text{H}_2\text{C}_2\text{O}_4$  in 10 ml solution + Equivalents of  $\text{NaHC}_2\text{O}_4$  in 10 ml solution

$$\begin{aligned}&= \frac{3 \times 0.1}{1000} \\ \frac{X \times 10}{45 \times 1000} + \frac{Y \times 10}{112 \times 1000} &= \frac{3 \times 0.1}{1000}\end{aligned}$$

$$112X + 45Y = \frac{3 \times 0.1 \times 45 \times 112}{10} = 151.2$$

..... (i)

### For redox reaction

$$\text{Equivalent mass of } \text{H}_2\text{C}_2\text{O}_4 = \frac{90}{2} = 45.$$

$$\text{Equivalent mass of } \text{NaHC}_2\text{O}_4 = \frac{112}{2} = 56$$

(Change in oxidation number of carbon per molecule = 2;  $\text{C}_2^{3+} \rightarrow 2\text{C}^{4+}$ )

Now,

Equivalents of  $\text{H}_2\text{C}_2\text{O}_4$  in 10 ml solution + Equivalents of  $\text{NaHC}_2\text{O}_4$  in 10 ml solution

$$= \frac{4 \times 0.1}{1000} .$$

$$\frac{X \times 10}{45 \times 1000} + \frac{Y \times 10}{56 \times 1000} = \frac{4 \times 0.1}{1000}$$

$$56X + 45Y = 100.8 \quad ..... (\text{ii})$$

On solving equations (i) and (ii), we get

$$X = 0.9 \text{ g}$$

$$Y = 1.12 \text{ g}$$

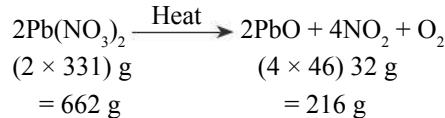
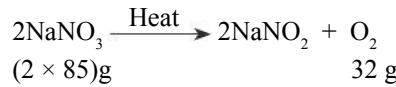
2. A solid mixture (5.0 g) consisting of lead nitrate and sodium nitrate was heated below  $600^\circ\text{C}$  until the mass of the residue was constant. If the loss in mass is 28.0 %. Find the amount of lead nitrate and sodium nitrate in the mixture.

[IIT 1990]

**Solution** Let the amount of  $\text{NaNO}_3$  in the mixture be 'X' g.

The amount of  $\text{Pb}(\text{NO}_3)_2$  in the mixture

$$= (5.0 - X) \text{ g.}$$



170 g of  $\text{NaNO}_3$  evolve oxygen = 32 g

$$X \text{ g of } \text{NaNO}_3 \text{ evolve oxygen} = \frac{32}{170} \times X \text{ g}$$

$$662 \text{ g of } \text{Pb}(\text{NO}_3)_2 \text{ evolve gas} = 216 \text{ g}$$

$$(50 - X) \text{ g of } \text{Pb}(\text{NO}_3)_2 \text{ evolve gas}$$

$$= \frac{216}{662} \times (5.0 - X) \text{ g}$$

## 1.26 ■ Mole Concept and Stoichiometry

$$\text{Total loss} = \frac{32}{170} X + \frac{216}{662} \times (5.0 - X)$$

$$\text{Loss given in the problem} = \frac{28}{100} \times 5 = 1.4 \text{ g}$$

$$\frac{32}{170} X + \frac{216}{662} (5.0 - X) = 1.4$$

On solving, we get

$$X = 1.676 \text{ g}$$

So mass of  $\text{NaNO}_3$  = 1.676 g

$$\begin{aligned}\text{Mass of } \text{Pb}(\text{NO}_3)_2 &= (5.0 - 1.676) \text{ g} \\ &= 3.324 \text{ g.}\end{aligned}$$

3. Calculate the molality of one litre solution of 93%  $\text{H}_2\text{SO}_4$  (weight/volume). The density of the solution is 1.84 g/ml.

[IIT 1990]

**Solution** Given,

93 %  $\text{H}_2\text{SO}_4$  solution (weight/volume)

It means 93 g of  $\text{H}_2\text{SO}_4$  present in 100 ml of solution, therefore

$$\text{Weight of } \text{H}_2\text{SO}_4 = 93 \text{ g}$$

$$\text{Volume of solution} = 100 \text{ ml}$$

$$\text{So weight of solution} = 100 \times 1.84 = 184 \text{ g}$$

$$\text{Weight of water} = 184 - 93 = 91 \text{ g}$$

$$\text{Molality} = \frac{\text{moles of } \text{H}_2\text{SO}_4}{\text{Weight of water in (g)}} \times 1000$$

$$\text{Moles of } \text{H}_2\text{SO}_4 = \frac{93}{98} = 0.948$$

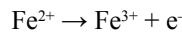
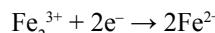
$$\text{So Molality} = \frac{0.948}{91} \times 1000 = 10.42$$

4. A 1.0 g sample of  $\text{Fe}_2\text{O}_3$  solid of 55.2 % purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made upto 100.0 ml. An aliquot of 25.0 ml of this solution requires for titration. Calculate the number of electrons taken up by the oxidant in the reaction of the above titration.

[IIT 1991]

**Solution** The redox changes are:

For reduction of  $\text{Fe}_2\text{O}_3$  by zinc dust



Oxidant + n  $e^-$  → Reductant

Meq. of  $\text{Fe}_2\text{O}_3$  in 25 ml

= Meq. of  $\text{Fe}^{3+}$  in  $\text{Fe}_2\text{O}_3$

= Meq. of  $\text{Fe}^{2+}$  formed

= Meq. of oxidant used to oxidize  $\text{Fe}^{2+}$

So Meq. of  $\text{Fe}_2\text{O}_3$  in 25 ml = Meq. of oxidant

$$= 17 \times 0.0167 \times n$$

Here 'n' is the number of electrons gained by 1 molecule of oxidant

So Meq. of  $\text{Fe}_2\text{O}_3$  in 100 ml

$$= 17 \times 0.0167 \times n \times \frac{100}{25}$$

$$\frac{1 \times 55.2 \times 1000}{100 \times M/2} = 17 \times 0.0167 \times n \times 4$$

As molecular weight of  $\text{Fe}_2\text{O}_3$  = 160

$$\text{So } n = \frac{1 \times 55.2 \times 2 \times 1000}{100 \times 160 \times 17 \times 0.0167 \times 4} = 6$$

Thus, number of electrons gained by one molecule of oxidant = 6.

5. A solution of 0.2 g of a compound containing  $\text{Cu}^{2+}$  and  $\text{C}_2\text{O}_4^{2-}$  ions on titration with 0.02 M  $\text{KMnO}_4$  in presence of  $\text{H}_2\text{SO}_4$  consumes 22.6 ml oxidant. The resulting solution is neutralized by  $\text{Na}_2\text{CO}_3$ , acidified with dilute acetic acid and titrated with excess of KI. The liberated iodine required 11.3 ml of 0.05 M  $\text{Na}_2\text{S}_2\text{O}_3$  for complete reduction. Find out the mole ratio of  $\text{Cu}^{2+}$  and  $\text{C}_2\text{O}_4^{2-}$  in the compound.

[IIT 1991]

**Solution**

**Ist Case**

Only  $\text{C}_2\text{O}_4^{2-}$  ions are oxidized by  $\text{KMnO}_4$  solution.

Normality of  $\text{KMnO}_4$  solution =  $0.02 \times 5 = 0.1 \text{ N}$

$$22.6 \text{ ml of } 0.1 \text{ N } \text{KMnO}_4 =$$

$$22.6 \text{ ml of } 0.1 \text{ N } \text{C}_2\text{O}_4^{2-} \text{ solution}$$

Mass of  $\text{C}_2\text{O}_4^{2-}$  ions in the solution

$$= \frac{N \times E \times V}{1000} = \frac{N \times M \times V}{1000 \times 2}$$

Number of moles of  $\text{C}_2\text{O}_4^{2-}$  ions in the solution

$$= \frac{N \times M \times V}{1000 \times 2 \times M}$$

$$= \frac{N \times V}{2000} = \frac{0.1 \times 22.6}{2000}$$

$$= 11.3 \times 10^{-4}$$

## IIInd Case

Only  $\text{Cu}^{2+}$  ions are reduced by KI and iodine liberated is neutralized by  $\text{Na}_2\text{S}_2\text{O}_3$  solution.

$$11.3 \text{ ml of } 0.05 \text{ M } \text{Na}_2\text{S}_2\text{O}_3$$

$$\equiv 11.3 \text{ ml of } 0.05 \text{ N } \text{Na}_2\text{S}_2\text{O}_3$$

$$= 11.3 \text{ ml of } 0.05 \text{ N I}_2$$

$$= 11.3 \text{ ml of } 0.05 \text{ N } \text{Cu}^{2+}$$

Mass of  $\text{Cu}^{2+}$  ions in the solution

$$= \frac{N \times E \times V}{100} = \frac{N \times M \times V}{1000}$$

Number of moles of  $\text{Cu}^{2+}$  ions in the solution

$$= \frac{N \times M \times V}{1000 \times M}$$

$$= \frac{N \times V}{1000} = \frac{0.05 \times 11.3}{1000}$$

$$= 5.65 \times 10^{-4}$$

$$\text{Molar ratio of } \frac{\text{Cu}^{2+}}{\text{C}_2\text{O}_4^{2-}} = \frac{5.65 \times 10^{-4}}{11.3 \times 10^{-4}} = \frac{1}{2}.$$

6. A 2.0 g sample of a mixture containing sodium carbonate, sodium bicarbonate and sodium sulphate is gently heated till the evolution of  $\text{CO}_2$  ceases. The volume of  $\text{CO}_2$  at 750 mm Hg pressure and at 298 K is measured to be 123.9 ml. A 1.5 g of the same sample requires 150 ml of (M/10) HCl for complete neutralization. Calculate the per cent composition of the components of the mixture.

[IIT 1992]

**Solution** According to ideal gas equation,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Volume of  $\text{CO}_2$  at NTP

$$(V_2) = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2}.$$

$$= \frac{750 \times 123.9}{298} \times \frac{273}{760}$$

$$= \frac{25368525}{226480} = 112 \text{ ml}$$

As weight of 22400 ml of  $\text{CO}_2$  at NTP = 44 g

So weight of 112 ml of  $\text{CO}_2$  at NTP

$$= \frac{44}{22400} \times 112 \text{ g}$$

$$= 0.22 \text{ g}$$

On heating a mixture of  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SO}_4$ , only  $\text{NaHCO}_3$  is decomposed according to following equation.



$$2(23+1+12+48) = 168$$

As 44 g  $\text{CO}_2$  is required = 168 g of  $\text{NaHCO}_3$

So 0.22 g  $\text{CO}_2$  is required

$$= \frac{168}{44} \times 0.22 \text{ g of NaHCO}_3$$

$$= 0.84 \text{ g of NaHCO}_3$$

As the weight of  $\text{NaHCO}_3$  in the mixture = 0.84

So the percentage of  $\text{NaHCO}_3$  in the mixture

$$= \frac{0.84}{2.0} \times 100 = 42.0 \%$$

When 1.5 g of mixture is treated with HCl. Therefore  $\text{Na}_2\text{SO}_4$  is not reacted while  $\text{Na}_2\text{CO}_3$  is reacted with HCl as follows:



$$2 \times 23 + 12 + 48 \quad 2(1 + 35.5)$$

$$= 106 \quad = 73$$



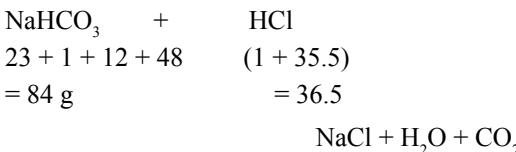
Let the amount of  $\text{Na}_2\text{CO}_3$  in 1.5 g of mixture be 'Y' g.

So the amount of HCl used with  $\text{Na}_2\text{CO}_3$

$$= \frac{73}{106} \times Y \text{ g}$$

## 1.28 ■ Mole Concept and Stoichiometry

$\text{NaHCO}_3$  reacts with HCl as follows:



Amount of HCl used with  $\text{NaHCO}_3$

$$\frac{36.5}{84} \times 0.63 = 0.2737 \text{ g}$$

Number of millimoles of HCl used with mixture

$$= \text{Molarity} \times \text{Volume in ml}$$

$$= \frac{1}{10} \times 150 = 15$$

Weight of HCl used with mixture

$$= \text{millimole} \times \text{mol. wt.} \times 10^{-3}$$

$$= 15 \times 10^{-3} \times 36.5 = 0.5475 \text{ g}$$

Total HCl = Used HCl with  $\text{Na}_2\text{CO}_3$

+ Used HCl with  $\text{NaHCO}_3$

$$0.5475 = \frac{75}{106} \times Y + 0.2737$$

On solving, we get

$$Y = 0.3975$$

So % of  $\text{Na}_2\text{CO}_3$  in the mixture

$$= \frac{0.3975}{1.5} \times 100 = 26.5 \%$$

% of  $\text{Na}_2\text{SO}_4$  in the mixture

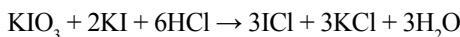
$$= 100 - \% \text{ of } \text{NaHCO}_3 - \% \text{ of } \text{Na}_2\text{CO}_3$$

$$= 100 - 42 - 26.5$$

$$= 31.5 \%$$

7. One gram of commercial  $\text{AgNO}_3$  is dissolved in 50 ml of water. It is treated with 50 ml of a KI solution. The silver iodide thus precipitated is filtered off. Excess of KI in the filtrate is titrated with (M/10)  $\text{KIO}_3$  solution in presence of 6 M HCl till all  $\text{I}^-$  ions are converted into  $\text{ICl}$ . It requires 50 ml of (M/10)  $\text{KIO}_3$  solution. 20 ml of the same stock solution of KI requires 30 ml of (M/10)  $\text{KIO}_3$  under similar conditions. Calculate the percentage of  $\text{AgNO}_3$  in the sample.

Reaction:



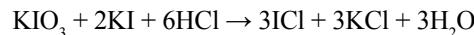
[IIT 1992]

**Solution** Number of millimoles of  $\text{KIO}_3$  in 30 ml of solution

$$= \text{Molarity} \times \text{Volume in ml}$$

$$= \frac{1}{10} \times 30 = 3$$

Equation:



According to the equation

1 mole of  $\text{KIO}_3$  is equivalent to 2 moles of KI

As Number of millimoles of KI in 20 ml of stock solution

$$= 2 \times 3 = 6$$

So, number of millimoles of KI in 50 ml of the

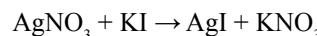
$$\text{same solution} = 6 \times \frac{50}{20} = 15$$

Number of millimoles of  $\text{KIO}_3$  in 50 ml of solution

$$= \frac{1}{10} \times 50 = 5$$

So number of millimoles of KI used with 50 ml of  $\text{KIO}_3$  solution =  $2 \times 5 = 10$

Number of millimoles of KI used with  $\text{AgNO}_3$  =  $15 - 10 = 5$



1 mole of  $\text{AgNO}_3$  reacts with 1 mole of KI. So number of millimoles of  $\text{AgNO}_3$  is equal to 5.

$$\text{Weight of } \text{AgNO}_3 = 5 \times 10^{-3} \times 170 \text{ g}$$

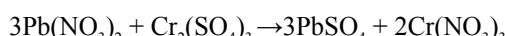
$$= 0.85 \text{ g}$$

$$\% \text{ of } \text{AgNO}_3 = \frac{0.85 \times 100}{1.0} = 85.0 \%$$

8. Upon mixing 45.0 ml of 0.25 M lead nitrate solution with 25 ml of 0.1 M chromic sulphate solution, precipitation of lead sulphate takes place. How many moles of lead sulphate are formed? Also calculate the molar concentrations of the species left behind in the final solution. Assume that lead sulphate is completely insoluble.

[IIT 1993]

**Solution** The reaction is



3 mole      1 mole      3 mole      2 mole

Number of moles of  $\text{Pb}(\text{NO}_3)_3$

$$= 45 \times 10^{-3} \times 0.25$$

$$= 11.25 \times 10^{-3} \text{ mole}$$

Number of moles of  $\text{Cr}_2(\text{SO}_4)_3$

$$= 25 \times 10^{-3} \times 0.1$$

$$= 2.5 \times 10^{-3} \text{ mole}$$

So  $\text{Cr}_2(\text{SO}_4)_3$  has limiting concentration. It will be consumed fully and the number of moles of lead sulphate produced will be

$$= 3 \times 2.5 \times 10^{-3} = 7.5 \times 10^{-3} \text{ mole}$$

Number of moles of lead nitrate left

$$= 11.25 \times 10^{-3} - 7.5 \times 10^{-3}$$

$$= 3.75 \times 10^{-3} \text{ mole}$$

$$\text{Total volume} = 45.0 + 25.0 = 70 \text{ ml}$$

$$= 70 \times 10^{-3} \text{ litre}$$

$$\text{Molarity} = \frac{3.75 \times 10^{-3}}{70 \times 10^{-3}} = 0.0536 \text{ M}$$

Number of moles of  $\text{Cr}(\text{NO}_3)_3$  formed

$$= 2 \times 2.5 \times 10^{-3} = 5 \times 10^{-3} \text{ mole}$$

$$\text{Molarity} = \frac{5 \times 10^{-3}}{70 \times 10^{-3}} = 0.0714 \text{ M}$$

$\text{Pb}(\text{NO}_3)_2$  and  $\text{Cr}(\text{NO}_3)_3$  will be present in solution in ionic form,

So,

$$[\text{Pb}^{2+}] = 0.0536 \text{ M}$$

$$[\text{Cr}^{3+}] = 0.0714 \text{ M}$$

$$[\text{NO}_3^-] = (2 \times 0.0536) + (3 \times 0.0714)$$

$$= 0.3214 \text{ M.}$$

9.  $8.0575 \times 10^{-2} \text{ kg}$  of Glauber's salt is dissolved in water to obtain  $1 \text{ dm}^3$  of a solution of density  $1077.2 \text{ kg m}^{-3}$ . Calculate the molarity, molality and mole-fraction of  $\text{Na}_2\text{SO}_4$  in the solution.

[IIT 1994]

**Solution** In  $1 \text{ dm}^3$  solution, weight of Glauber's salt

$$(\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}) = 8.0575 \times 10^{-2} \text{ kg}$$

Mass of solution = Volume  $\times$  density

$$= 1 \text{ dm}^3 \times 1077.2 \times 10^{-3} \text{ kg dm}^{-3}$$

$$= 1.0772 \text{ kg}$$

So in solution weight of solvent

$$= \text{Weight of solution} - \text{Wt. of Glauber's salt}$$

$$= 1.0772 - 0.080575$$

$$= 0.996625 \text{ kg}$$

Molarity of solution

$$= \frac{\text{Weight of } \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O in g}}{\text{dm}^3 / \text{mol. wt. of } \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}}$$

$$= \frac{80.575 \text{ g/dm}^3}{322} = 0.250 \text{ M}$$

Molality of solution

$$= \frac{\text{Molarity of solution}}{\text{Weight of solvent in kg/dm}^3} \cdot$$

$$= \frac{0.250}{1.0772} = 0.232 \text{ m}$$

$$\text{Moles of solvent (water)} = \frac{996.625}{18} = 55.34$$

$$\text{Moles of } \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = \frac{80.575}{322} = 0.250$$

Mole fraction of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

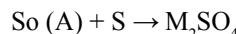
$$= \frac{\text{Moles of } \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}}{\text{Total moles}}$$

$$= \frac{55.34}{55.34 + 0.25} = 0.995$$

10. 'A' is a binary compound of a univalent metal.  $1.422 \text{ g}$  of (A) reacts  $1.743 \text{ g}$  of a white crystalline solid (B), that forms a hydrated double salt (C) with  $\text{Al}_2(\text{SO}_4)_3$ . Identify (A), (B) and (C).

[IIT 1994]

**Solution** Compound (B) form hydrated crystals with  $\text{Al}_2(\text{SO}_4)_3$ . As (B) is formed with univalent metal on heating with sulphur. So compound (B) should be  $\text{M}_2\text{SO}_4$ , so compound (A) must be oxide of M which reacts with sulphur to give  $\text{M}_2\text{SO}_4$ .



As  $1.422 \text{ g}$  of (A) reacts with  $0.321 \text{ g}$  of sulphur completely and gives  $1.743 \text{ g}$  of  $\text{M}_2\text{SO}_4$ .

## 1.30 ■ Mole Concept and Stoichiometry

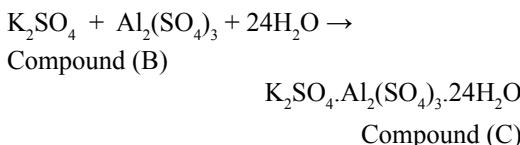
$$\text{So } 32.1 \text{ g of S will give} = \frac{1.743 \times 32.1}{0.321} \\ = 174.3 \text{ g}$$

As molecular wt. of  $\text{M}_2\text{SO}_4$  = 173.4

$$\text{So } 2 \times (\text{A}) + 32.1 + 64 = 1723.4$$

$$\text{So } (\text{A}) \text{ (atomic weight of M)} = 39$$

Monovalent metal is K (as at. wt. of K is 39)



As 0.321 g of sulphur react with 1.422 g of (A)

So 32.1 g of sulphur react with

$$\frac{1.422 \times 32.1}{0.321} \text{ g of (A)} = 142.2 \text{ g}$$



142.2 g wt. is related to two moles of  $\text{MO}_x$  or  $\text{KO}_x$ .

$$2 [39 + 16X] = 142.2$$

$$78 + 32X = 142.2$$

$$X = 2$$

So compound (A) is  $\text{KO}_2$  (Potassium superoxide) which is a binary compound.

Compound (A) =  $\text{KO}_2$

Compound (B) =  $\text{K}_2\text{SO}_4$

Compound (C) =  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

11. The composition of a sample of wustite is  $\text{Fe}_{0.93}\text{O}_{100}$ . What percentage of the iron is present in the form of Fe(III)?

[IIT 1994]

**Solution** Let the percentage of Fe(III) be X and Fe(II) would be  $(100 - X)$ .

Number of oxygen molecules in  $\text{Fe}_2\text{O}_3$  =  $(3/2)X$

Total iron atoms =  $100 - X + X = 100$

$$\text{Total oxygen atoms} = (3/2)X + 100 - X \\ = 100 + (X/2)$$

$$\text{Ratio} = \frac{0.93}{1.00} = \frac{100}{100 + (X/2)}$$

$$93 \times 0.465 X = 100$$

$$X = 15.05$$

$$X = 15.05 \%$$

12. A mixture of ethane and ethene occupies 40 litre at 1.00 atm and at 400 K. The mixture reacts completely with 130 g of  $\text{O}_2$  to produce  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Assuming ideal gas behaviour, find the mole fractions of  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_4$  in the mixture.

[IIT 1995]

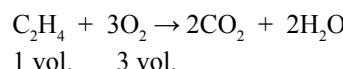
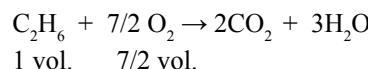
**Solution** Volume of the mixture at NTP

$$= \frac{40 \times 1}{400} \times \frac{273}{1} = 27.3 \text{ litre}$$

Suppose the volume of ethane is X litre.

$$\text{Volume of ethene} = (273 - X) \text{ litre}$$

Equations:



Total volume of oxygen required for complete combustion of the mixture is:

$$[ \frac{7}{2} X + (27.3 - X) \times 3 ] \text{ litre}$$

$$\text{or } \frac{[7X + (27.3 - X) \times 6]}{2} \text{ litre}$$

$$\text{Mass of oxygen} = \frac{[7X + (27.3 - X) \times 6]}{2} \times \frac{32}{22.4} .$$

$$130 = (X + 163.8) \times \frac{16}{22.4} .$$

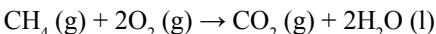
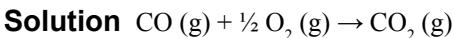
$$X = 18.2$$

$$\text{So, mole fraction of ethane} = \frac{18.2}{27.3} \times 100 \\ = 66.66$$

$$\text{Mole fraction of ethene} = 33.34$$

13. A 20.0 cm<sup>3</sup> mixture of CO, CH<sub>4</sub> and He gases is exploded by an electric discharge at room temperature with excess of oxygen. The volume contraction is found to be 13.0 cm<sup>3</sup>. A further contraction of 14.0 cm<sup>3</sup> occurs when the residual gas is treated with KOH solution. Find out the composition of the gaseous mixture in terms of volume percentage.

[IIT 1995]



Suppose 'X' is the volume of CO 'Y' is the volume of CH<sub>4</sub>

$$\frac{1}{2}X + Y = 13 \quad \dots\dots 1.$$

$$X + Y = 14$$

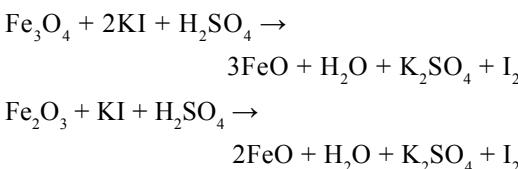
$$X = 10 \text{ cc and } Y = 4 \text{ cc}$$

$$\text{So \% CH}_4 = 20, \% \text{ CO} = 50, \% \text{ He} = 30$$

14. A 3.0 g sample containing Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and an inert impure substance is treated with excess of KI solution in presence of dilute H<sub>2</sub>SO<sub>4</sub>. The entire iron is converted to Fe<sup>2+</sup> along with the liberation of iodine. The resulting solution is diluted to 100 ml. A 20 ml of the dilute solution requires 11.0 ml of 0.5 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution to reduce the iodine present. A 50 ml of the diluted solution after complete extraction of iodine requires 12.8 ml of 0.25 M KMnO<sub>4</sub> solution in dilute H<sub>2</sub>SO<sub>4</sub> medium for oxidation of Fe<sup>2+</sup>. Calculate the percentage of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> in the original sample.

[IIT 1996]

**Solution** Fe<sub>3</sub>O<sub>4</sub> is an equimolar mixture of Fe<sub>2</sub>O<sub>3</sub> and FeO. Thus, the sample contains Fe<sub>2</sub>O<sub>3</sub>, FeO and impurities. The amount of iodine liberated depends on the amount of Fe<sub>2</sub>O<sub>3</sub> and the entire iron is converted into Fe<sup>2+</sup>.



$$\begin{aligned} &5 \times 11.0 \text{ ml of } 0.5 \text{ M Na}_2\text{S}_2\text{O}_3 \\ &\equiv 55.0 \text{ ml of } 0.5 \text{ N Na}_2\text{S}_2\text{O}_3 \text{ solution} \\ &\equiv 55.0 \text{ ml of } 0.5 \text{ N I}_2 \text{ solution} \\ &\equiv 55.0 \text{ ml of } 0.5 \text{ N Fe}_2\text{O}_3 \text{ solution} \\ &= 27.5 \times 10^{-3} \text{ eq. Fe}_2\text{O}_3 \text{ solution} \\ &= 13.75 \times 10^{-3} \text{ moles Fe}_2\text{O}_3 \end{aligned}$$

$$\begin{aligned} &2 \times 12.8 \text{ ml of } 0.25 \text{ M KMnO}_4 \text{ solution} \\ &\equiv 25.6 \text{ ml of } 1.25 \text{ N KMnO}_4 \text{ solution} \\ &\equiv 25.6 \text{ ml of } 1.25 \text{ N FeO solution} \\ &= 32.0 \times 10^{-3} \text{ equivalent FeO} \\ &= 32.0 \times 10^{-3} \text{ moles FeO} \end{aligned}$$

$$\begin{aligned} \text{Moles of FeO in Fe}_3\text{O}_4 &= 0.032 - 0.0275 \\ &= 0.0045 \end{aligned}$$

$$\text{Mass of Fe}_3\text{O}_4 = 0.0045 \times 232 = 1.044 \text{ g}$$

$$\begin{aligned} \text{Moles of Fe}_2\text{O}_3 \text{ existing separately} \\ &= 0.01375 - 0.0045 = 0.00925 \end{aligned}$$

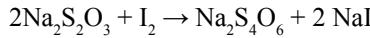
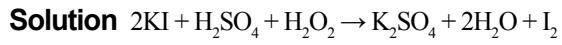
$$\text{Mass of Fe}_2\text{O}_3 = 0.00925 \times 160 = 1.48 \text{ g}$$

$$\% \text{ Fe}_3\text{O}_4 = \frac{1.044}{3} \times 100 = 34.8$$

$$\% \text{ Fe}_2\text{O}_3 = \frac{1.48}{3} \times 100 = 49.33$$

15. To a 25 ml H<sub>2</sub>O<sub>2</sub> solution, excess of acidified solution of potassium iodide was added. The iodine liberated required 20 ml of 0.3 N sodium thiosulphate solution. Calculate the volume strength of H<sub>2</sub>O<sub>2</sub> solution.

[IIT 1997]



$$\begin{aligned} \text{Meq. of Na}_2\text{S}_2\text{O}_3 &= 20 \times 0.3 = 6 \\ &\quad (\text{Normality} \times \text{volume}) \end{aligned}$$

$$\text{Meq. of Na}_2\text{S}_2\text{O}_3 = \text{Meq. of I}_2 = 6$$

$$\text{Meq. of I}_2 = \text{Meq. of H}_2\text{O}_2 = 67$$

## 1.32 ■ Mole Concept and Stoichiometry

$$\begin{aligned}\text{Weight of H}_2\text{O}_2 &= \text{Meq.} \times E \times 10^{-3} \\ &= 6 \times 17 \times 10^{-3} = 0.102 \text{ g}\end{aligned}$$

(As eq. wt. of H<sub>2</sub>O<sub>2</sub> = 34/2 = 17)

$$\begin{aligned}\text{Strength of H}_2\text{O}_2 &= 0.102 \times \frac{1000}{25} \\ &= 0.408 \text{ g/L}\end{aligned}$$

$$\begin{aligned}\text{Molarity of H}_2\text{O}_2 &= \frac{0.408 \text{ g} \cdot \text{L}}{\text{Mol. wt. (34)}} \\ &= 0.012 \text{ M}\end{aligned}$$

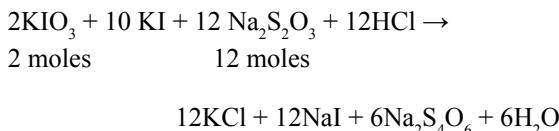
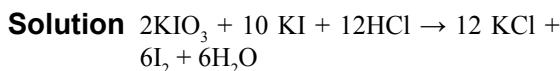
2H <sub>2</sub> O <sub>2</sub>	$\rightarrow$	2H <sub>2</sub> O	+	O <sub>2</sub>
2 moles				1 mole
0.012 moles				0.06 moles

$$\begin{aligned}\text{So volume of O}_2 \text{ at STP} &= 0.06 \times 22.4 \text{ L} \\ &= 1.344 \text{ L}\end{aligned}$$

So the volume strength of H<sub>2</sub>O<sub>2</sub> = 1.344 L

16. An aqueous solution containing 0.10 g KIO<sub>3</sub> (formula weight = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated iodine consumed 45.0 ml of thiosulphate solution to decolorize the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution.

[IIT 1998]



$$\text{Number of moles of KIO}_3 = \frac{0.10}{214}$$

$$\begin{aligned}\text{Number of moles of} &\quad 0.10/214 \text{ moles of} \\ \text{Na}_2\text{S}_2\text{O}_3 \text{ required for} &\quad \text{KIO}_3 \\ &= \frac{12}{2} \times \frac{0.10}{214} = \frac{0.60}{214}\end{aligned}$$

$$\begin{aligned}\text{Molarity of Na}_2\text{S}_2\text{O}_3 &= \frac{0.6}{214} \times \frac{1000}{45} \\ &= 0.0623 \text{ M}\end{aligned}$$

17. How many millilitres of 0.5 M H<sub>2</sub>SO<sub>4</sub> are needed to dissolve 0.5 g of copper (II) carbonate?

[IIT 1999]



$$N_1 = \text{Normality of H}_2\text{SO}_4 = 0.5 \times 2 = 1 \text{ N}$$

$$V_1 = \text{Volume of H}_2\text{SO}_4$$

$$N_2 = \text{Normality of copper (II) carbonate}$$

$$= \frac{0.5 \times 2}{123.5} \text{ N}$$

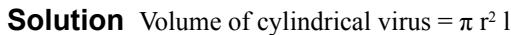
$$\begin{aligned}V_2 &= \text{Volume of copper (II) carbonate} \\ &= 1000 \text{ ml}\end{aligned}$$

$$\text{So } 1.0 \times V_1 = \frac{0.5 \times 2}{123.5} \times 1000$$

$$V_1 = 8.09 \text{ ml}$$

18. A plant virus is found to consist of uniform cylindrical particles of 150 Å in diameter and 5000 Å long. The specific volume of the virus is 0.75 cm<sup>3</sup>/g. If the virus is considered to be a single particle, calculate its molecular mass.

[IIT 1999]



$$= 3.14 \times (\frac{150}{2} \times 10^{-8})^2 \times 5000 \times 10^{-8}$$

$$= 0.884 \times 10^{-16} \text{ cm}^3$$

$$\text{Mass of virus} = \frac{\text{Volume}}{\text{Specific volume}}$$

$$= \frac{0.884 \times 10^{-16}}{0.75} = 1.178 \times 10^{-16} \text{ g}$$

Molar mass of virus

$$= \text{Mass of single virus} \times 6.023 \times 10^{23}$$

$$= 1.178 \times 10^{-16} \times 6.023 \times 10^{23}$$

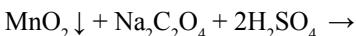
$$= 7.095 \times 10^7.$$

19. Hydrogen peroxide solution (20 ml) reacts quantitatively with a solution of  $\text{KMnO}_4$  (20 ml) acidified with dilute  $\text{H}_2\text{SO}_4$ . The same volume of the  $\text{KMnO}_4$  solution is just decolorized by 10 ml of  $\text{MnSO}_4$  in neutral medium simultaneously forming a dark brown precipitate of hydrated  $\text{MnO}_2$ . The brown precipitate is dissolved in 10 ml of 0.2 M sodium oxalate under boiling condition in the presence of dilute  $\text{H}_2\text{SO}_4$ . Write the balanced equations involved in the reactions and calculate the molarity of  $\text{H}_2\text{O}_2$ .

[IIT 2001]

### Solution

(i)



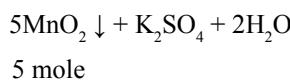
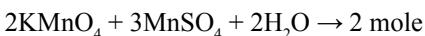
1 mole 1 mole



$$\text{mM of MnO}_2 = \text{mM of Na}_2\text{C}_2\text{O}_4$$

$$= 10 \times 0.2 = 2$$

(ii)



$$\text{mM of KMnO}_4 = \text{mM of MnO}_2 \times \frac{2}{5} .$$

$$= 2 \times \frac{2}{5} = \frac{4}{5} .$$

(iii)



mole 5 mole



$$\text{mM of H}_2\text{O}_2 = \text{mM of KMnO}_4 \times \frac{5}{2}$$

$$= \frac{4}{5} \times \frac{5}{2} = 2$$

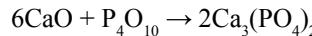
$$\text{M} \times 20 = 2$$

$$\text{M}(\text{H}_2\text{O}_2) = \frac{2}{20} = 0.1 \text{ M}$$

20. How many grams of  $\text{CaO}$  are required to neutralize 852 g of  $\text{P}_4\text{O}_{10}$ ?

[IIT 2005]

**Solution** The reaction is as follows:



$$852 \text{ g P}_4\text{O}_{10} \equiv 3 \text{ mol P}_4\text{O}_{10}$$

As 1 mole of  $\text{P}_4\text{O}_{10}$  neutralizes 6 moles of  $\text{CaO}$ .

So 3 moles of  $\text{P}_4\text{O}_{10}$  will neutralize 18 moles of  $\text{CaO}$ .

Mass of  $\text{CaO} = 18 \times 56 = 1008 \text{ g}$ .

21. 20 % surface sites have adsorbed  $\text{N}_2$ . On heating  $\text{N}_2$  gas evolved from sites and were collected at 0.001 atm and 298 K in a container of volume is  $2.46 \text{ cm}^3$ . Density of surface sites is  $6.023 \times 10^{14}/\text{cm}^2$  and surface area is  $1000 \text{ cm}^2$ , find out the number of surface sites occupied per molecule of  $\text{N}_2$ .

[IIT 2005]

**Solution** Density of surface site =  $6.023 \times 10^{14} \text{ cm}^{-2}$

Total surface area =  $1000 \text{ cm}^2$

Total number of surface sites

= Density  $\times$  Total surface area

$$= 6.023 \times 10^{14} \times 1000$$

$$= 6.023 \times 10^{17}$$

Sites occupied by nitrogen molecule (20%)

$$= \frac{20}{100} \times 6.023 \times 10^{17} = 1.2046 \times 10^{17}$$

$$\text{Number of nitrogen molecule} = \frac{\text{PV}}{\text{RT}} \times \text{NA}$$

$$\text{T} = 298 \text{ K}, \text{PP} = 0.001 \text{ atm}$$

$$\text{V} = 2.46 \text{ cm}^3 = 2.46 \times 10^{-3} \text{ L}$$

$$\text{R} = 0.0821 \text{ L-atm/K/mol}$$

Number of nitrogen molecule

$$= \frac{0.001 \times 2.46 \times 10^{-3}}{0.0821 \times 298} \times 6.023 \times 10^{23}$$

$$= 6.02 \times 10^{16}$$

Thus number of sites occupied by each nitrogen molecule

$$= \frac{\text{Sites occupied by N}_2 \text{ molecules}}{\text{Number of N}_2 \text{ molecules}}$$

$$= \frac{1.2046 \times 10^{17}}{6.02 \times 10^{16}} = 2$$

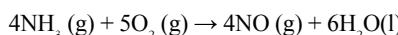
## MULTIPLE-CHOICE QUESTIONS

### Straight Objective Type Questions (Single Choice only)

1. If 0.50 mole of  $\text{BaCl}_2$  is mixed with 0.20 mol of  $\text{Na}_3\text{PO}_4$ , the maximum number of moles of  $\text{Ba}_3(\text{PO}_4)_2$  that can be formed is
  - a. 0.10
  - b. 0.20
  - c. 0.30
  - d. 0.40
2. One mole of  $\text{N}_2\text{H}_4$  loses ten moles of electrons to form a new compound Y. Assuming that all the nitrogen appears in the new compound, what is the oxidation state of nitrogen in Y? (There is no change in the oxidation state of hydrogen).
  - a. +2
  - b. -2
  - c. +3
  - d. +4
3. The equivalent weight of  $\text{MnSO}_4$  is half its molecular weight when it is converted to
  - a.  $\text{MnO}$
  - b.  $\text{MnO}_4^{2-}$
  - c.  $\text{MnO}_2$
  - d.  $\text{MnO}_4^-$
4. In which mode of expression, the concentration of a solution remains independent of temperature?
  - a. Formality
  - b. Molality
  - c. Molarity
  - d. Normality
5. One litre hard water contains 12.00 mg  $\text{Mg}^{2+}$ . Milliequivalents of washing soda required to remove its hardness is
  - a. 1
  - b. 12.16
  - c.  $1 \times 10^{-3}$
  - d.  $12.16 \times 10^{-3}$
6. At STP the density of  $\text{CCl}_4$  vapour in g/l will be nearest to
  - a. 8.67
  - b. 6.87
  - c. 5.67
  - d. 4.26
7. 1 c.c.  $\text{N}_2\text{O}$  at NTP contains
  - a.  $\frac{1.8}{224} \times 10^{22}$  atoms
  - b.  $\frac{6.02}{22400} \times 10^{23}$  molecules
  - c.  $\frac{1.32}{224} \times 10^{23}$  electrons
  - d. all of above

8. The volume strength of 1.5 N  $\text{H}_2\text{O}_2$  solution is:
  - a. 3.0
  - b. 4.8
  - c. 8.0
  - d. 8.4
9. The number of gram-molecule of oxygen which contain  $6.02 \times 10^{24}$   $\text{CO}$  molecules is
  - a. 10 g molecule
  - b. 5 g molecule
  - c. 1 g molecule
  - d. 0.5 g molecule
10. The mass of  $1 \times 10^{22}$  molecules of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is
  - a. 41.59 g
  - b. 415.9 g
  - c. 4.159 g
  - d. none of these
11. The weight of one molecule of a compound  $\text{C}_{60}\text{H}_{122}$  is
  - a.  $1.2 \times 10^{-20}$  gm
  - b.  $1.4 \times 10^{-21}$  gm
  - c.  $5.025 \times 10^{23}$  gm
  - d.  $6.023 \times 10^{23}$  gm
12. The percentage weight of Zn in white vitriol  $[\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}]$  is approximately equal to (Zn = 65, S = 32, O = 16 and H = 1)
  - a. 33.65 %
  - b. 32.56 %
  - c. 23.65%
  - d. 22.65%
13. The volume of carbon dioxide gas evolved at STP by heating 7.3 gm of  $\text{Mg}(\text{HCO}_3)_2$  will be
  - a. 1100 ml
  - b. 1120 ml
  - c. 2230 ml
  - d. 3240 ml
14. The amount of Zinc (atomic weight = 65) necessary to produce 224 ml of  $\text{H}_2$  by the reaction with an acid will be
  - a. 0.65 gm
  - b. 7.6 gm
  - c. 6.5 gm
  - d. 8.5 gm
15. Number of atoms in 4.25 gm of  $\text{NH}_3$  is approximately
  - a.  $6 \times 10^{23}$
  - b.  $15 \times 10^{23}$
  - c.  $1.5 \times 10^{23}$
  - d.  $2.5 \times 10^{23}$
16. The number of molecules in 4.25 g of ammonia is
  - a.  $1.5 \times 10^{23}$
  - b.  $2.5 \times 10^{23}$
  - c.  $3.5 \times 10^{23}$
  - d.  $15 \times 10^{23}$
17. The weight of a single atom of oxygen is
  - a.  $5.057 \times 10^{-23}$  g
  - b.  $1.556 \times 10^{-23}$  g
  - c.  $2.656 \times 10^{-23}$  g
  - d.  $4.538 \times 10^{-23}$  g

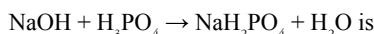
18. In the reaction



when 1 mole of ammonia and 1 mole of  $\text{O}_2$  are made to react to completion

- a. 1.0 mole of  $\text{H}_2\text{O}$  is produced
- b. 1.0 mole of NO will be produced
- c. all the oxygen will be consumed
- d. all the ammonia will be consumed

19. The equivalent weight of phosphoric acid ( $\text{H}_3\text{PO}_4$ ) in the reaction:



- a. 89
- b. 98
- c. 59
- d. 29

20. Assuming fully decomposed, the volume of  $\text{CO}_2$  released at STP on heating 9.85 g of  $\text{BaCO}_3$  (atomic mass, Ba = 137) will be

- a. 2.24 l
- b. 4.96 l
- c. 1.12 l
- d. 0.84 l

21. What is the volume (in litres) of  $\text{CO}_2$  liberated at STP, when 2.12 gram of sodium carbonate (mol. wt. = 106) is treated with excess dilute HCl?

- a. 11.2
- b. 2.12
- c. 0.448
- d. 4.26

22. Percentage of Se in peroxidase anhydrase enzyme is 0.5 % by weight (at. wt. = 78.4) then minimum molecular weight of peroxidase anhydrase enzyme is

- a.  $1.568 \times 10^3$
- b. 15.68
- c.  $2.136 \times 10^4$
- d.  $1.568 \times 10^4$

23. What is the volume (in litres) of oxygen at STP required for complete combustion of 32 g of  $\text{CH}_4$  (mol. wt. of  $\text{CH}_4$  = 16)

- a. 89.6
- b. 189.6
- c. 98.4
- d. 169.5

24. How many water molecules are there in one drop of water (volume 0.0018 ml) at room temperature?

- a.  $4.86 \times 10^{17}$
- b.  $6.023 \times 10^{24}$
- c.  $2.584 \times 10^{19}$
- d.  $6.023 \times 10^{19}$

25. The weight of one molecule of a compound  $\text{C}_{60}\text{H}_{122}$  is

- a.  $1.3 \times 10^{-20}$  g
- b.  $5.01 \times 10^{-21}$  g
- c.  $3.72 \times 10^{23}$  g
- d.  $1.4 \times 10^{-21}$  g

26. 3 g of an oxide of a metal is converted to chloride completely and it yielded 5 g of chloride. The equivalent weight of the metal is

- a. 3.325
- b. 13.25
- c. 23.52
- d. 33.25

27. In Haber process, 30 litres of dihydrogen and 30 litres of dinitrogen were taken for reaction which yielded only 50% of the expected product. What will be the composition of gaseous mixture under the aforesaid condition in the end?

- a. 20 litres ammonia, 25 litres nitrogen, 15 litres hydrogen
- b. 20 litres ammonia, 20 litres nitrogen, 20 litres hydrogen
- c. 10 litres ammonia, 25 litres nitrogen, 15 litres hydrogen
- d. 20 litres ammonia, 10 litres nitrogen, 30 litres hydrogen

28. 25 ml of a solution of barium hydroxide on titration with 0.1 molar solution of hydrochloric acid gave a titre value of 35 ml. The molarity of barium hydroxide solution was

- a. 0.07
- b. 0.14
- c. 0.28
- d. 0.35

29. What volume of hydrogen gas, at 273 K and 1 atm pressure will be consumed in obtaining 21.6 g of elemental boron (atomic mass = 10.8) from the reduction of boron trichloride by hydrogen?

- a. 89.6 L
- b. 67.2 L
- c. 44.8 L
- d. 22.4 L

30. A compound has haemoglobin like structure. It has one Fe. It contains 4.6 % of Fe. The approximate molecular mass is

- a.  $1400 \text{ g mol}^{-1}$
- b.  $1000 \text{ g mol}^{-1}$
- c.  $1100 \text{ g mol}^{-1}$
- d.  $1200 \text{ g mol}^{-1}$

31. The maximum number of molecules is present in

- a. 15 L of  $\text{H}_2$  gas at STP
- b. 5 L of  $\text{N}_2$  gas at STP
- c. 0.5 g of  $\text{H}_2$  gas
- d. 10 g of  $\text{O}_2$  gas

32. To neutralize completely 20 ml of 0.1 M aqueous solution of phosphorus acid, the volume of 0.1 M aqueous KOH solution required is

- a. 10 ml
- b. 40 ml
- c. 60 ml
- d. 80 ml

33.  $6.02 \times 10^{20}$  molecules of urea are present in 100 ml of its solution. The concentration of urea solution is

## 1.36 ■ Mole Concept and Stoichiometry

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| <p>a. 0.02 M                    b. 0.001 M</p> <p>c. 0.01 M                    d. 0.1 M</p> <p><b>34.</b> g of <math>\text{CaCO}_3</math> is completely decomposed to X and <math>\text{CaO}</math>. X is passed into an aqueous solution containing one mole of sodium carbonate. What is the number of moles of sodium bicarbonate formed?<br/>(mol. wt. of <math>\text{CaCO}_3</math> = 100, <math>\text{Na}_2\text{CO}_3</math> = 106, <math>\text{NaHCO}_3</math> = 84)</p> <p>a. 0.010                    b. 0.2</p> <p>c. 0.4                        d. 10</p> <p><b>35.</b> An organic compound containing C and H has 92.3% of carbon. Its empirical formula is</p> <p>a. <math>\text{CH}_4</math>                    b. <math>\text{CH}_3</math></p> <p>c. <math>\text{CH}_2</math>                    d. <math>\text{CH}</math></p> <p><b>36.</b> 4 g of copper was dissolved in concentrated nitric acid. The copper nitrate on strong heating gave 5 g of its oxide. The equivalent weight of copper is</p> <p>a. 12                        b. 16</p> <p>c. 32                        d. 34</p> <p><b>37.</b> A gas mixture contains 50 % helium and 50 % methane by volume. What is the per cent by weight of methane in the mixture?</p> <p>a. 83 %                    b. 73.0 %</p> <p>c. 18.01 %                d. 80.0 %</p> <p>e. 90.1 %</p> <p><b>38.</b> Number of water molecules in the drop of water, if 1 ml of water has 20 drops and 'A' is Avogadro's number, is</p> <p>a. 0.5 A                    b. 0.5 A/18</p> <p>c. 0.05 A/18              d. 0.05 A</p> <p><b>39.</b> The mass of carbon anode consumed (giving only carbon dioxide) in the production of 270 kg of aluminium metal from bauxite by the Hall process is (at. mass of Al = 27)</p> <p>a. 270 kg                  b. 540 kg</p> <p>c. 90 kg                    d. 180 kg</p> <p><b>40.</b> 100 g <math>\text{CaCO}_3</math> is treated with 1 litre of N HCl. What would be the weight of <math>\text{CO}_2</math> liberated after the completion of the reaction?</p> <p>a. 11 g                    b. 22 g</p> <p>c. 33 g                    d. 44 g</p> <p>e. 5.5 g</p> <p><b>41.</b> An alkaloid contains 17.28 % of nitrogen and its molecular mass is 162. The number of nitrogen atoms present in one molecule of the alkaloid is</p> | <p>a. One                      b. Two</p> <p>c. Three                    d. Four</p> <p>e. Five</p> <p><b>42.</b> If 30 ml of <math>\text{H}_2</math> and 20 ml of <math>\text{O}_2</math> react to form water, what is left at the end of the reaction?</p> <p>a. 5 ml of <math>\text{O}_2</math>              b. 5 ml of <math>\text{H}_2</math></p> <p>c. 10 ml of <math>\text{O}_2</math>             d. 10 ml of <math>\text{H}_2</math></p> <p><b>43.</b> Density of a 2.05 M solution of acetic acid in water is 1.02 g/ml. The molality of the solution is</p> <p>a. 1.14 mol <math>\text{kg}^{-1}</math>        b. 3.28 mol <math>\text{kg}^{-1}</math></p> <p>c. 2.28 mol <math>\text{kg}^{-1}</math>        d. 0.44 mol <math>\text{kg}^{-1}</math></p> <p><b>44.</b> The decomposition of a certain mass of <math>\text{CaCO}_3</math> gave 11.2 dm<sup>3</sup> of <math>\text{CO}_2</math> gas at STP. The mass of KOH required to completely neutralize the gas is</p> <p>a. 56 g                    b. 28 g</p> <p>c. 42 g                    d. 20 g</p> <p><b>45.</b> One mole of acidified <math>\text{K}_2\text{Cr}_2\text{O}_7</math> on reaction with excess KI will liberate ..... moles (s) of <math>\text{I}_2</math></p> <p>a. 2                        b. 3</p> <p>c. 6                        d. 7</p> <p><b>46.</b> <math>\text{KMnO}_4</math> (mol. wt. = 158) oxidizes oxalic acid in acidic medium to <math>\text{CO}_2</math> and water as follows.<br/><math display="block">5\text{C}_2\text{O}_4^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \rightarrow 10\text{CO}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}</math>What is the equivalent weight of <math>\text{KMnO}_4</math>?</p> <p>a. 158                    b. 31.6</p> <p>c. 39.5                    d. 79</p> <p><b>47.</b> 500 ml of <math>\text{NH}_3</math> contains <math>6.0 \times 10^{23}</math> molecules at STP. How many molecules are present in 100 ml of <math>\text{CO}_2</math> at STP?</p> <p>a. <math>6 \times 10^{23}</math>            b. <math>1.5 \times 10^{23}</math></p> <p>c. <math>1.2 \times 10^{23}</math>          d. none of these</p> <p><b>48.</b> In the reaction, <math>4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}</math>, when one mole of ammonia and one mole of oxygen are made to react to completion, then</p> <p>a. 1.0 mole of <math>\text{H}_2\text{O}</math> is produced</p> <p>b. all the oxygen is consumed</p> <p>c. 1.5 mole of NO is formed</p> <p>d. all the ammonia is consumed</p> <p><b>49.</b> 4 moles each of <math>\text{SO}_2</math> and <math>\text{O}_2</math> gases are allowed to react to form <math>\text{SO}_3</math> in a closed vessel. At equilibrium, 25 % of <math>\text{O}_2</math> is used up. The total number of moles of all the gases at equilibrium is</p> <p>a. 2.0                    b. 6.0</p> <p>c. 7.0                    d. 8.0</p> |
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- 50.** 1.520 g of hydroxide of a metal on ignition gave 0.995 g of oxide. The equivalent weight of the metal is  
 a. 0.995      b. 190  
 c. 1.90      d. 9
- 51.** The molarity of the solution obtained by dissolving 2.5 g of NaCl in 100 ml of water is  
 a. 0.427 moles      b. 427 moles  
 c. 0.0472 moles      d. 0.00427 moles
- 52.** 0.532 gram of chloroplatinate of an organic base (mol. wt. 244) gave 0.195 gram of platinum on ignition. The number of nitrogen atoms per molecule of base is  
 a. 4      b. 3  
 c. 2      d. 1
- 53.** One litre solution containing 490 g of sulphuric acid is diluted to 10 litres with water. What is the normality of the resulting solution?  
 a. 1.0 N      b. 10.0 N  
 c. 0.5 N      d. 5.0 N
- 54.** An element, X has the following isotopic composition;  
 $^{200}\text{X}$  : 90 %  
 $^{199}\text{X}$  : 8.0 %  
 $^{202}\text{X}$  : 2.0 %  
 The weighted average atomic mass of the naturally occurring element X is closest to  
 a. 200 amu      b. 201 amu  
 c. 202 amu      d. 199 amu
- 55.** The crystalline salt  $\text{Na}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$  on heating loses 55.9 % of its weight. The formula of the crystalline salt is  
 a.  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$   
 b.  $\text{Na}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$   
 c.  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$   
 d.  $\text{Na}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$   
 e.  $\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$
- 56.** 10 litres of  $\text{O}_2$  gas is reacted with 30 litres of CO at STP. The volume of each gas present at the end of the reaction are  
 a.  $\text{O}_2 = 10$  litres, CO = 30 litres  
 b.  $\text{O}_2 = 10$  litres,  $\text{CO}_2 = 20$  litres  
 c. CO = 10 litres,  $\text{CO}_2 = 20$  litres  
 d. CO = 20 litres,  $\text{CO}_2 = 10$  litres  
 e.  $\text{O}_2 = 10$  litres, CO = 10 litres
- 57.** 0.3 g of an acid is neutralized by 40 cm<sup>3</sup> of 0.125 N NaOH. Equivalent mass of the acid is  
 a. 20      b. 60  
 c. 30      d. 46
- 58.** 5 g of  $\text{CaCO}_3$  completely reacts with  
 a. 3.65 g of HCl  
 b. 7.35 g of HCl  
 c. 36.5 g of HCl  
 d. 0.365 g of HCl
- 59.** Sodium nitrates on reduction with Zn in presence of NaOH solution produces  $\text{NH}_3$ . Mass of sodium nitrate absorbing 1 mole of electron will be  
 a. 5.550      b. 10.625  
 c. 9.000      d. 9.876
- 60.** In transforming 0.01 mole of PbS to  $\text{PbSO}_4$  the volume of '10 volume'  $\text{H}_2\text{O}_2$  required will be  
 a. 10.3      b. 22.7  
 c. 23.0      d. 44.8
- 61.** An unknown element forms an oxide. What will be the equivalent weight of the element if the oxygen content is 20% by weight?  
 a. 14      b. 32  
 c. 2      d. 54
- 62.** 2 N HCl solution will have same molar conc. as a  
 a. 4.0 N  $\text{H}_2\text{SO}_4$       b. 1 N  $\text{H}_2\text{SO}_4$   
 c. 0.5 N  $\text{H}_2\text{SO}_4$       d. 2 N  $\text{H}_2\text{SO}_4$
- 63.** Number of moles of  $\text{MnO}_4^-$  required to oxidize one mole of ferrous oxalate completely in acidic medium will be  
 a. 7.5 moles      b. 0.2 moles  
 c. 0.6 moles      d. 0.4 moles
- 64.** How many grams of carbon dioxide can form when a mixture of 4.95 g ethylene ( $\text{C}_2\text{H}_4$ ) and 3.25 g of oxygen is ignited, assuming complete combustion to form carbon dioxide and water?  
 a. 5.96 g      b. 1.49 g  
 c. 1.98 g      d. 2.98 g
- 65.** Hardness of water sample is 300 ppm  $\text{CaCO}_3$ . Hence its molarity is  
 a. 0.30 M      b. 0.003 M  
 c. 0.030 M      d. 0.0013 M

### Brainteasers Objective Type Questions (Single choice only)

66. Specific volume of cylindrical virus particle is  $6.02 \times 10^{-2}$  cc/gm. Whose radius and length 7 Å and 10 Å respectively. If  $N_A = 6.02 \times 10^{23}$ , find the molecular weight of virus.
- $3.08 \times 10^3$  kg/mol
  - $3.08 \times 10^4$  kg/mol
  - $1.54 \times 10^4$  kg/mol
  - 15.4 kg/mol
67. A 6.977 g sample of a mixture was analysed for barium ion by adding a small excess of sulphuric acid to an aqueous solution of the sample. The resultant reaction produced a precipitate of barium sulphate, which was collected by filtration, washed, dried and weighed. If 0.4123 g of barium sulphate was obtained, what was the mass percentage of barium in the sample?
- 6.952 %
  - 3.476 %
  - 4.376 %
  - 1.738 %
68. Volume occupied by one molecule of water (density = 1 g cm<sup>-3</sup>) is
- $3.0 \times 10^{-23}$  cm<sup>3</sup>
  - $5.5 \times 10^{-23}$  cm<sup>3</sup>
  - $9.0 \times 10^{-23}$  cm<sup>3</sup>
  - $6.023 \times 10^{-23}$  cm<sup>3</sup>
69. In the reaction,
- $$\text{Al (s)} + 6\text{HCl (aq)} \rightarrow$$
- $$2\text{Al}^{3+} (\text{aq}) + 6\text{Cl}^- (\text{aq}) + 3\text{H}_2 (\text{g})$$
- a. 33.6 L H<sub>2</sub> (g) is produced regardless of temperature and pressure for every mole Al that reacts
- b. 67.2 L H<sub>2</sub> (g) at STP is produced for every mole Al that reacts
- c. 11.2 L H<sub>2</sub> (g) at STP is produced for every mole HCl (aq) consumed.
- d. 6 L HCl (aq) is consumed for every 3L H<sub>2</sub> (g) produced.
70. How many grams of calcium hydroxide, Ca(OH)<sub>2</sub>, must be dissolved in water to give 250.0 millilitres of 0.0200 M Ca(OH)<sub>2</sub> solution?
- 0.37 gm
  - 3.76 gm
  - 0.185 gm
  - 0.74 gm

71. For the formation of 3.65 g of hydrogen chloride gas, what volumes of hydrogen gas and chlorine gas are required at NTP conditions?
- 1 lit, 1 lit
  - 1.12 lit, 2.24 lit
  - 3.65 lit, 1.83 lit
  - 1.12 lit, 1.12 lit
72. A metal oxide has the formula Z<sub>2</sub>O<sub>3</sub>. It can be reduced by hydrogen to give free metal and water 0.1596 g of the metal oxide requires 6 mg of hydrogen for complete reduction. The atomic weight of the metal is
- 27.9
  - 159.6
  - 79.8
  - 55.8
73. 61.5 gm of a saturated solution (at 25°C) of a divalent metal sulphate is made upto 250 ml. 25 ml of this made up solution produces 1.375 gm of dry BaSO<sub>4</sub> with excess BaCl<sub>2</sub>. The solubility of the metal sulphate at 25°C in gm per 100 g of water is (Ba = 137; S = 32; O = 16 ; MSO<sub>4</sub> = 148)
- 14.6
  - 17.6
  - 16.6
  - 19.6
74. Liquid benzene (C<sub>6</sub>H<sub>6</sub>) burns in oxygen according to
- $$2\text{C}_6\text{H}_6 (\text{l}) + 15\text{O}_2 (\text{g}) \rightarrow 12\text{CO}_2 (\text{g}) + 6\text{H}_2\text{O}(\text{g})$$
- How many litres of O<sub>2</sub> at STP are needed to complete the combustion of 39 g of liquid benzene? (Mol. wt. of O<sub>2</sub> = 32, C<sub>6</sub>H<sub>6</sub> = 78)
- 74 L
  - 11.2 L
  - 22.4 L
  - 84 L
75. 3.92 g of ferrous ammonium sulphate are dissolved in 100 ml of water. 20 ml of this solution requires 18 ml of potassium permanganate during titration for complete oxidation. The weight of KMnO<sub>4</sub> present in one litre of the solution is
- 13.47 g
  - 3.476 g
  - 14.76 g
  - 34.78 g
76. The number of oxalic acid molecules in 100 ml of 0.02 N oxalic acid solution is
- $6.023 \times 10^{22}$
  - $10^{-3}$
  - $6.022 \times 10^{20}$
  - none
77. The advantage of using KO<sub>2</sub> as gas masks in spaceships is that it absorbs CO<sub>2</sub>, at the same time releasing oxygen. If 0.001 mole of KO<sub>2</sub> is present in an atmosphere containing 22.4 cm<sup>3</sup> of CO<sub>2</sub> at STP

- free from moisture, what will be the volume of  $O_2$  released at STP?
- a. 16.8 cm<sup>3</sup>      b. 18.6 cm<sup>3</sup>  
 c. 18.8 cm<sup>3</sup>      d. 17.8 cm<sup>3</sup>
78. Rearrange the following (I to IV) in the order of increasing masses and choose the correct answer from (a), (b), (c) and (d) (At. mass : N = 14, O = 16, Cu = 63)
- I. 1 molecule of O  
 II. 1 atom of nitrogen  
 III.  $1 \times 10^{-10}$  g molecular mass of oxygen  
 IV.  $1 \times 10^{-7}$  g atomic mass of copper
- a. II < I < III < IV  
 b. IV < III < II < I  
 c. II < III < I < IV  
 d. III < IV < I < II
79. How many moles of lead (II) chloride will be formed from a reaction between 6.5 g of PbO and 3.2 g of HCl?
- a. 0.011      b. 0.029  
 c. 0.044      d. 0.333
80. In the photographic developing process, silver bromine is dissolved by adding sodium thiosulphate:
- $$AgBr(s) + 2Na_2S_2O_3(aq) \rightarrow Na_3Ag(S_2O_3)_2(aq) + NaBr(aq)$$
- If you want to dissolve 0.250 g of AgBr, what volume of 0.0138 M  $Na_2S_2O_3$ , in milliliters, should be used?
- a. 143 ml      b. 139 ml  
 c. 96.5 ml      d. 193 ml
81. A mixture of 0.002 mole of  $KBrO_3$  and 0.01 mole of KBr was treated with excess of KI and acidified. The volume of 0.1 M  $Na_2S_2O_3$  solution required to consume the liberated iodine will be
- a. 150 ml      b. 90 ml  
 c. 120 ml      d. 100 ml
82. A sample was analysed and reported to contain 20 % NaOH. Later it was found that the basic material is KOH rather than NaOH. The percentage KOH in the sample is
- a. 42.9      b. 19.4  
 c. 21      d. 29.4
83. The percentage of an element M is 53 in its oxide of molecular formula  $M_2O_3$ . Its atomic mass is about
- a. 54      b. 32  
 c. 27      d. 41
84. 0.2g of a sample of an oxalate salt is dissolved in 100 cc of water. It required 90 cc of N/20  $KMnO_4$  solution for complete oxidation. The percentage of oxalate ( $C_2O_4^{2-}$ ) in the given sample is
- a. 33      b. 66  
 c. 26      d. 96
85. For the reaction  $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ , the volume of carbon monoxide required to reduce one mole of ferric oxide is
- a. 67.2 dm<sup>-1</sup>      b. 44.8 dm<sup>-1</sup>  
 c. 21.5 dm<sup>2</sup>      d. 89.7 dm<sup>1</sup>
86. The mass percentage of chloride ion in a 25.00 ml sample of sea water was determined by titrating the sample with silver nitrate, causing precipitation of silver chloride. If required 42.58 ml of 0.2997 M silver nitrate solution to reach the equivalence point in the titration. What is the mass percentage of chloride ion in the sea water if its density is 1.025 g/ml?
- a. 2.676 %      b. 0.883 %  
 c. 1.766 %      d. 3.766 %
87. Like many metals, aluminium also reacts with a halogen to give a metal halide
- $$2Al(s) + 3Br_2(l) \rightarrow Al_2Br_6(s)$$
- What quantity of  $Br_2$  (in grams) is required for complete reaction with 2.56 g of Al?
- What mass of white, solid  $Al_2Br_6$  is expected respectively?
- a.  $Br_2 = 11.2$  gm,  $Al_2Br_6 = 25.3$  gm  
 b.  $Br_2 = 22.7$  gm,  $Al_2Br_6 = 15.3$  gm  
 c.  $Br_2 = 22.7$  gm,  $Al_2Br_6 = 25.3$  gm  
 d.  $Br_2 = 11.2$  gm,  $Al_2Br_6 = 50.6$  gm
88. Study the following table:
- | Compound<br>(mol. wt.) | Wt. of compound<br>(in gm) taken |
|------------------------|----------------------------------|
| I. $CO_2$ (44)         | 4.4                              |
| II. $NO_2$ (46)        | 2.3                              |
| III. $H_2O_2$ (34)     | 6.8                              |
| IV. $SO_2$ (64)        | 1.6                              |

## 1.40 ■ Mole Concept and Stoichiometry

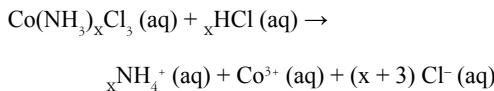
Which two compounds have least weight of oxygen

- a. I and II
- b. I and III
- c. II and IV
- d. III and IV

89.  $\text{MnO}_4^-$  ions are reduced in acidic condition to  $\text{Mn}^{2+}$  ions whereas they are reduced in neutral condition to  $\text{MnO}_2$ . The oxidation of 25 ml of a solution X containing  $\text{Fe}^{2+}$  ions required in acidic condition 20 ml of a solution Y containing  $\text{MnO}_4^-$  ions. What volume of solution Y would be required to oxidize 25 ml of solution X containing  $\text{Fe}^{2+}$  ions in neutral condition?

- a. 10.4 ml
- b. 12.89 ml
- c. 33.3 ml
- d. 23.9 ml

90. Cobalt (III) ion forms many compounds with ammonia. To find the formula of one of these compounds, you titrate the  $\text{NH}_3$  in the compound with standardized acid.



Assume that 23.63 ml of 1.500 M HCl is used to titrate 1.580 g of  $\text{Co}(\text{NH}_3)_x\text{Cl}_3$ . What is the value of X?

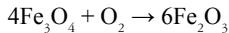
- a.  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
- b.  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$
- c.  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
- d.  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

91. A mixture of 0.5 g of ethanol and acetaldehyde when heated with Fehling's solution gave 1.2 g of red precipitate of  $\text{Cu}_2\text{O}$ .

What is the percentage of acetaldehyde in the mixture?

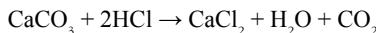
- a. 54 %
- b. 47 %
- c. 74 %
- d. 36 %

92. If 70.0 g of  $\text{Fe}_3\text{O}_4$  and 12.0 g of  $\text{O}_2$  are present in a reaction mixture, determine how many grams of each reactant will be left unreacted upon completion of the following reaction.



- a. Zero g  $\text{Fe}_3\text{O}_4$  and 6.9 g  $\text{O}_2$
- b. Zero g  $\text{Fe}_3\text{O}_4$  and 9.6 g  $\text{O}_2$
- c. 6.9 g  $\text{Fe}_3\text{O}_4$  and 9.6 g  $\text{O}_2$
- d. 9.6 g  $\text{Fe}_3\text{O}_4$  and zero g  $\text{O}_2$

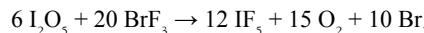
93.  $\text{CaCO}_3$  is decomposed by HCl (density 1.825 g/cc)



Volume of HCl required to decompose 10 g of 50% pure  $\text{CaCO}_3$  is:

- a. 1.22 ml
- b. 2.0 ml
- c. 0.242 ml
- d. 3.2 ml

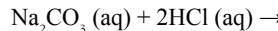
94. The reaction between 113.4 g of  $\text{I}_2\text{O}_5$  and 132.2 g of  $\text{BrF}_3$  was found to produce 97.0 g of  $\text{IF}_5$ . The equation for the reaction is



What is the per cent yield of  $\text{IF}_5$ ?

- a. 37.7 %
- b. 75.4 %
- c. 150.8 %
- d. 57.4 %

95. What volume of 0.955 M HCl, in milliliters, is needed to titrate 2.152 g of  $\text{Na}_2\text{CO}_3$  to the equivalence point?



- a. 4.25 ml
- b. 21.5 ml
- c. 84.0 ml
- d. 42.5 ml

96. Ammonia gas can be prepared by the following reaction:



If 103 g of ammonia is obtained, but the theoretical yield is 136 g, what is the per cent yield of this gas?

- a. 75.7 %
- b. 25.1 %
- c. 57.5 %
- d. 15.7 %

97. The allowable concentration level of vinyl chloride,  $\text{C}_2\text{H}_3\text{Cl}$ , in the atmosphere in a chemical plant is  $2.0 \times 10^{-6}$  g/L. How many molecules are present per litre?

- a.  $1.47 \times 10^{16}$  m/L
- b.  $1.97 \times 10^{16}$  m/L
- c.  $2.97 \times 10^{16}$  m/L
- d.  $1.07 \times 10^{16}$  m/L

98. 0.7 g of a sample of  $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$  were dissolved in water and the volume was made to 100 ml. 20 ml of this solution required 19.8 ml of N/10 HCl for complete neutralization. The value of 'x' is:

- a. 3
- b. 2
- c. 4
- d. 6

99. A mixture (15 ml) of CO and  $\text{CO}_2$  is mixed with V ml (excess) of oxygen and electrically sparked.

The volume after explosion was  $(V + 12)$  ml, what would be the residual volume if 25 ml of the original mixture is exposed to alkali

- |                 |                 |
|-----------------|-----------------|
| <b>a.</b> 10 ml | <b>b.</b> 9 ml  |
| <b>c.</b> 8 ml  | <b>d.</b> 12 ml |
- 100.** An element A is converted to its bromide and the bromine precipitated as  $\text{AgBr}$ . Atomic weight of A = 91.2. 0.722 g of the bromide gives 1.32 g of  $\text{AgBr}$ . Valency of the element A is ( $\text{Ag} = 108$ ;  $\text{Br} = 80$ )
- |             |             |
|-------------|-------------|
| <b>a.</b> 2 | <b>b.</b> 3 |
| <b>c.</b> 4 | <b>d.</b> 5 |

### Multiple Correct Answer Type Questions

- 101.** 1 mole of  $\text{Mg}(\text{OH})_2$  can exactly neutralize
- a.** 1 mole  $\text{HNO}_3$
  - b.** 2 mole of  $\text{H}_3\text{PO}_2$
  - c.** 1 mole of  $\text{H}_2\text{SO}_4$
  - d.** 1 mole of  $\text{H}_3\text{PO}_3$
- 102.** A solution of  $\text{Na}_2\text{S}_2\text{O}_3$  is iodometrically titrated against 0.25050 g of  $\text{KBrO}_3$ . This process requires 90 ml of  $\text{Na}_2\text{S}_2\text{O}_3$  solution the strength of the  $\text{Na}_2\text{S}_2\text{O}_3$  is
- |                  |                 |
|------------------|-----------------|
| <b>a.</b> 0.2 M  | <b>b.</b> 0.1 M |
| <b>c.</b> 0.05 M | <b>d.</b> 0.1 N |
- 103.** The iodide content of a solution was determined by titration with cerium (IV) sulphate in the presence of HCl, in which  $\text{I}^-$  is converted to  $\text{ICl}$ . A 250 ml sample of the solution required 20 ml of 0.05 N  $\text{Ce}^{4+}$  solution. What is the iodide concentration in the original solution?
- a.**  $2 \times 10^{-5}$  moles
  - b.** 0.254 g/litre
  - c.**  $2.54 \times 10^{-2}$  moles
  - d.** 0.508 g/lit
- 104.** 3.16 g of  $\text{KMnO}_4$  is dissolved in water and the solution is made upto 1 litre. An unknown salt containing 6.88 g  $\text{Fe}^{2+}$  ion was dissolved in water and solution was made upto 100 ml. It was found that 20 ml of salt solution decolourised 27.25 ml of the above permanganate solution. Which of the following statements are correct?
- a.** normality of ferrous ion = 0.15 N
  - b.** actual strength of ferrous ion 68.8 g  $\text{lit}^{-1}$

- c.** percentage of ferrous ion is 10.58
  - d.** normality of ferrous ion is 0.13 N
- 105.**  $\text{H}_3\text{BO}_3$ , Boric acid is
- a.** Aprotic acid
  - b.** dibasic acid
  - c.** tribasic acid
  - d.** monobasic acid
- 106.** An aqueous solution containing 288 g of a non-electrolyte compound having the stoichiometric composition  $\text{C}_n\text{H}_{2n}\text{O}_n$  in 90 g water boils at 101.24°C and 1 atm pressure.  $K_b = 0.512 \text{ K mol}^{-1} \text{ kg}$ . Which of the following statements are correct?
- (i) molecular mass of  $\text{C}_n\text{H}_{2n}\text{O}_n = 1321.2 \text{ g}$
  - (ii) molecular formula of  $\text{C}_n\text{H}_{2n}\text{O}_n = \text{C}_{44}\text{H}_{88}\text{O}_{44}$
  - (iii) molecular mass of  $\text{C}_n\text{H}_{2n}\text{O}_n = 104.2 \text{ g}$
  - (iv) empirical formula of  $\text{C}_n\text{H}_{2n}\text{O}_n$  is  $\text{CH}_2\text{O}$
- |                      |                       |
|----------------------|-----------------------|
| <b>a.</b> (i) & (iv) | <b>b.</b> (ii) & (iv) |
| <b>c.</b> (i) & (ii) | <b>d.</b> (iv) & (ii) |
- 107.** 1.66 g KI reacts with excess of  $\text{KIO}_3$  to produce  $\text{I}_2$ , which converts  $\text{Na}_2\text{S}_2\text{O}_3$  into  $\text{SO}_4^{2-}$ . If the hypo solution was decimolar, then the volume required to reach equivalent point will be
- |                       |                 |
|-----------------------|-----------------|
| <b>a.</b> 0.015 litre | <b>b.</b> 15 ml |
| <b>c.</b> 0.02 litre  | <b>d.</b> 20 ml |
- 108.** Which of the following is/are incorrect for 17 g / l of  $\text{H}_2\text{O}_2$  solution?
- a.** The normality of solution is 3 M
  - b.** Volume strengths is 5.6 at 273 K and 1 atm
  - c.** 1 mL of this solution gives 1.4 mL  $\text{O}_2$  at 273 K and 2 atm
  - d.** Molarity of solution is 0.1 M
- 109.** Mole fraction of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) in ethanol-water system is 0.25. Thus it has:
- a.** 46 % ethanol by weight of solution
  - b.** 54 % water by weight of solution
  - c.** 25 % ethanol by weight of solution
  - d.** 75 % water by weight of solution
- 110.** In diammonium hydrogen phosphate,  $(\text{NH}_4)_2\text{HPO}_4$ , percentage as:
- a.** P is maximum
  - b.** N is maximum
  - c.**  $\text{P}_2\text{O}_5$  is 53.78 %
  - d.**  $\text{NH}_3$  is 25.76 %

## 1.42 ■ Mole Concept and Stoichiometry

111. A certain compound has the molecular formula  $X_4O_6$  having 57.2 % X. Thus:
- X can be a non-metal
  - X is an electropositive metal
  - Atomic mass of X is 32.
  - X may contain five valence electrons.
112. Which one of the following statements is/are correct?
- One mole of  $CH_4$  and 17 g  $NH_3$  at NTP occupies same volume
  - One gram mole of silver equals  $108/6.023 \times 10^{23}$  g
  - One gram mole of  $CO_2$  is  $6.023 \times 10^{23}$  times heavier than one molecule of  $CO_2$
  - One mole Ag weighs more than that of two moles of Ca
113. 1 g atom of oxygen can have
- 22.4 litre of  $O_2$  at N.T.P.
  - $6.02 \times 10^{23} O_2$  molecules
  - 16 g of  $O_2$
  - 11.2 litre of  $O_2$  at N.T.P.
114. For the reaction
- $$H_3PO_4 + Mg(OH)_2 \rightarrow CaHPO_4 + 2H_2O$$
- 1 mole 1 mole
- Then which of the following statement are correct?
- 1 mole of  $H_3PO_4$  is completely neutralized by 1 mole of  $Mg(OH)_2$
  - 1 mole of  $H_3PO_4$  is completely neutralized by 1.5 mole of  $Mg(OH)_2$
  - the equivalent weight of  $H_3PO_4$  is 49.
  - the resulting solution is neutralized by 1 mole of NaOH
115. Which of the following have same number of atoms?
- 22.4 L of  $O_2$  at STP
  - 5.0 g of He
  - 1.7 gm of  $NH_3$
  - 6.4g of  $O_2$
116. Consider the given reaction and select the correct statements.
- $$N_2 + 3H_2 \rightarrow 2NH_3$$
- a. the mass of ammonia formed when 2 kg.  $N_2$  react with 1 kg  $H_2$  is 2.428 gm.  
b. the mass of ammonia formed when 2 kg.  $N_2$  react with 1 kg  $H_2$  is 4.856 gm.  
c.  $H_2$  remain unreacted also and the mass left unreacted is 0.571 kg.  
d.  $H_2$  remain unreacted also and the mass left unreacted is 0.4286 kg.

### Linked-Comprehension Type Questions

#### Comprehension 1

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/ molecules (approximately  $6.023 \times 10^{23}$ ) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolyzed. This leads to the evolution of chlorine gas at one of the electrodes (atomic masses: Na = 23, Hg = 200, 1 Faraday = 96500 coulombs).

117. The total number of moles of chlorine gas evolved is

- a. 0.5                          b. 1.0  
c. 2.0                           d. 3.0

[IIT 2007]

118. If the cathode is a Hg electrode, the maximum weight (g) of amalgam formed from this solution is

- a. 200                           b. 225  
c. 400                           d. 446

[IIT 2007]

119. The total charge (coulombs) required for complete electrolysis is

- a. 24125                        b. 48250  
c. 96500                        d. 193000

[IIT 2007]

#### Comprehension 2

Oleum is considered as a solution of  $SO_3$  in  $H_2SO_4$ , which can be obtained by passing  $SO_3$  in solution of  $H_2SO_4$ . When 100 g sample of oleum is diluted with desired weight of  $H_2O$  then the total mass of  $H_2SO_4$  obtained after dilution is called as % labeling in oleum.

For example, an oleum bottle labeled as ‘118 % H<sub>2</sub>SO<sub>4</sub>’ means the 118 g total mass of pure H<sub>2</sub>SO<sub>4</sub> will be formed when 100g of oleum is diluted by 18 g of H<sub>2</sub>O which combines with all the free SO<sub>3</sub> present in oleum to form H<sub>2</sub>SO<sub>4</sub> as SO<sub>3</sub> + H<sub>2</sub>O → H<sub>2</sub>SO<sub>4</sub>.

120. What is the % of free SO<sub>3</sub> is an oleum that is labelled as ‘109 % H<sub>2</sub>SO<sub>4</sub>’?

a. 10                          b. 40  
c. 20                          d. 9

121. 4.5 g water is added into oleum sample labeled as “106% H<sub>2</sub>SO<sub>4</sub>” then the amount of free SO<sub>3</sub> remaining in the solution is :

a. 1.493 L at STP  
b. 1.792 L at STP  
c. 3.73 L at STP  
d. 1.12 L at STP

122. If excess water is added into a bottle sample labeled as “112 % H<sub>2</sub>SO<sub>4</sub>” and is reacted with 1.06 g Na<sub>2</sub>CO<sub>3</sub>, then find the volume of CO<sub>2</sub> evolved at 1 atm pressure and 300 K temperature after completion of the reaction :

a. 2.4615 L                    b. 24.6 L  
c. 0.24615 L                d. 12.3 L

123. 1 g of volume sample is diluted with water. The solution required 27 mL of 0.8 N NaOH for complete neutralization. The %v of free SO<sub>3</sub> in the sample is :

a. 74                            b. 26  
c. 20                            d. 80

### Comprehension 3

The strength of H<sub>2</sub>O<sub>2</sub> is expressed in many ways like molarity, normality, % (w / V), volume strength, etc. The strength of “15 V” means 1 volume of H<sub>2</sub>O<sub>2</sub> on decomposition gives 15 volumes of oxygen at STP or 1 litre of H<sub>2</sub>O<sub>2</sub> gives 15 litre of O<sub>2</sub> at STP. The decomposition of H<sub>2</sub>O<sub>2</sub> can be shown as follows:



H<sub>2</sub>O<sub>2</sub> can act as oxidizing as well as a reducing agent, as an oxidizing agent H<sub>2</sub>O<sub>2</sub> converts into H<sub>2</sub>O and as a reducing agent H<sub>2</sub>O<sub>2</sub> converts into O<sub>2</sub>, in both these cases it's n- factor is 2.

Hence normality of H<sub>2</sub>O<sub>2</sub> solution = 2 × Molarity of H<sub>2</sub>O<sub>2</sub> solution

124. What is the molarity of “16.8 V” of H<sub>2</sub>O<sub>2</sub> ?

a. 1.5 M                      b. 1 M  
c. 5.6 M                      d. 0.5 M

125. 25 ml of H<sub>2</sub>O<sub>2</sub> solution were added to excess of acidified solution of KI. The iodine so liberated required 20 ml of 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> for titration. Calculate the strength of H<sub>2</sub>O<sub>2</sub> in terms of normality.

a. 0.04                        b. 0.08  
c. 0.06                        d. 0.12

126. 10 ml. of H<sub>2</sub>O<sub>2</sub> solution is reacted with 40 ml of KMnO<sub>4</sub> in acidic medium then what is the volume strength of H<sub>2</sub>O<sub>2</sub> ?

a. 2.8                        b. 5.6  
c. 11.2                        d. 8.4

127. What is the percentage strength (% w/ V) of “16.8 V” H<sub>2</sub>O<sub>2</sub> ?

a. 1.7                        b. 5.1  
c. 34                        d. 1.68

### Comprehension 4

A redox reaction involves oxidation and reduction simultaneously by exchange of electrons. The species undergoing oxidation and reduction are reductant and oxidant respectively. In order to get n -factor or any oxidant or reductant change of oxidation number is first find out.

128. The ion X<sup>n+</sup> is oxidized to XO<sup>-</sup> by MnO<sub>4</sub><sup>-</sup> giving Mn<sup>2+</sup> in acid solution. Given that  $2.68 \times 10^{-3}$  mole of X<sup>n+</sup> requires  $1.61 \times 10^{-3}$  mole of MnO<sub>4</sub><sup>-</sup>, what is the value of n? What is the wt. of one g. equivalent of XCl<sub>n</sub> for the above reaction if the atomic mass of X is 97.0?

a. 80                        b. 84  
c. 168                        d. 72

129. How many gram HCl can be oxidized into free chlorine by 40 g. of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in an acidic solution, the latter being reduced to Cr<sup>+3</sup> ions?

$$(\text{Cr} = 52, \text{K} = 39, \text{O} = 16)$$

a. 29.579                    b. 29.785  
c. 29.795 gm.              d. 29. 859

130. Which of the following is not correct here

a. For the reaction



$$E_{\text{Cu}_2\text{S}} = M/8$$

b. a Cu<sub>2</sub>O + bNO<sub>3</sub><sup>-</sup> + 14H<sup>+</sup> → Cu<sup>2+</sup> + NO + 7H<sub>2</sub>O

Here a : b is 3 : 2

c. FeS<sub>2</sub> → Fe<sub>2</sub>O<sub>3</sub> + SO<sub>2</sub>

$$\text{Here E} = \frac{M}{11}$$

d. The value of n- factor of Fe(SCN)<sub>2</sub> when it oxidizes into Fe<sup>+3</sup>, SO<sub>4</sub><sup>-2</sup> and (CN)<sub>2</sub> is 12

**Assertion-Reason Type Questions**

In the following question two statements (Assertion) A and Reason (R) are given. Mark.

- a. if A and R both are correct and R is the correct explanation of A;
  - b. if A and R both are correct but R is not the correct explanation of A;
  - c. A is true but R is false;
  - d. A is false but R is true;
  - e. A and R both are false.
131. (A): One mole of NaCl contains  $6.023 \times 10^{23}$  molecules of sodium chloride.  
 (R): 58.5 g of NaCl also contains  $6.023 \times 10^{23}$  molecules of NaCl.
132. (A): 22.4 L of N<sub>2</sub> at NTP and 5.6 L O<sub>2</sub> at NTP contain equal number of molecules.  
 (R): Under similar conditions of temperature and pressure all gases contain equal number of molecules.
133. (A): Number of gm-molecules of SO<sub>2</sub>Cl<sub>2</sub> in 13.5 g of sulphuryl chloride is 0.2.  
 (R): Gram molecules is equal to those molecules which are expressed in gram.
134. (A): In CO molecule 12 parts by mass of carbon combine with 16 parts by mass of oxygen and in CO<sub>2</sub>, 12 parts by mass of carbon combine with 32 parts by mass of oxygen.  
 (R): When two elements combine separately with a fixed mass or a third element, then the ratio of their masses in which they do so is either the same or whole number multiple of the ratio in which they combine with each other.
135. (A): The molality of the solution does not change with change in temperature.  
 (R): The molality is expressed in units of moles per 1000 gm of solvent.
136. (A): Molarity of a solution and molality of a solution both change with density  
 (R): Density of the solution changes when percentage by mass of solution changes.
137. (A): The percentage of nitrogen in urea is 46.6 %.  
 (R): Urea is ionic compound.
138. (A): 0.28 g of N<sub>2</sub> has equal volume as 0.44 g of another gas at same conditions of temperature and pressure.  
 (R): molecular mass of another gas is 44 g mol<sup>-1</sup>.

139. (A): In MnO<sub>4</sub><sup>-</sup> + 5Fe<sup>2+</sup> + 8H<sup>+</sup> → Mn<sup>2+</sup> + 5Fe<sup>3+</sup> + 4H<sub>2</sub>O, MnO<sub>4</sub><sup>-</sup> acts as oxidizing agent and Fe<sup>2+</sup> acts as reducing agent.  
 (R): The reactions involving simultaneous loss or gain of electron among the reacting species are called oxidation reduction reactions.
140. (A): Equivalent mass of a base which contains one mole of replaceable OH<sup>-</sup> ion in a molecule.  
 (R): It is the mass of a base which completely reacts with one gram equivalent mass of an acid.
141. (A): Decomposition of H<sub>2</sub>O<sub>2</sub> is a disproportionation reaction.  
 (R): H<sub>2</sub>O<sub>2</sub> molecule simultaneously undergoes both oxidation and reduction.
142. (A): Molarity of a solution and molality of a solution both change with density.  
 (R): Density of the solution changes when percentage by mass of solution changes.
143. (A): The molality of the solution does not change with change in temperature.  
 (R): The molality is expressed in units of moles per 1000g of solvent.
144. (A): In the balanced redox reaction x Cu<sub>2</sub>O + y NO<sub>3</sub><sup>-</sup> + 14 H<sup>+</sup> → 6Cu<sup>2+</sup> + NO + 7H<sub>2</sub>O, the n-factor of Cu<sub>2</sub>O and NO<sub>3</sub><sup>-</sup> is 2 and 3 respectively.  
 (R): Since reciprocal of n-factor's ratio is molar ratio and so, x : y = 3 : 2
145. (A): For the reaction  

$$\text{Na}_2\text{CO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{NaHCO}_3$$
 The equivalent weight of Na<sub>2</sub>CO<sub>3</sub> is 106.  
 (R): Because the n-factor Na<sub>2</sub>CO<sub>3</sub> is 1 and equivalent weight =  

$$\frac{\text{molecular weight}}{\text{n-factor}}$$
146. (A): A bottle is labeled as "10 V" of H<sub>2</sub>O<sub>2</sub>. So its percentage strength is 5%.  
 (R): % strength of H<sub>2</sub>O<sub>2</sub> is nothing but it is the number of grams of H<sub>2</sub>O<sub>2</sub> in 100 mL solution of H<sub>2</sub>O<sub>2</sub> and it is related with volume strength as under 1 "vol" of H<sub>2</sub>O<sub>2</sub> = 0.303 %.

**Matrix-Match Type Questions**

**147.** Match the following:

Column I	Column II
A. 1.12 L CO <sub>2</sub>	(p) 0.5 N <sub>A</sub> molecules
B. 0.8 gm CH <sub>4</sub>	(q) 0.05 N <sub>A</sub> molecules
C. 11.2 L SO <sub>2</sub>	(r) 0.15 N <sub>A</sub> atoms
D. 16 gm O <sub>2</sub>	(s) N <sub>A</sub> no. of oxygen atoms

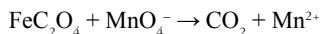
**148.** Match the following:

List I (Reaction)	List II (Maximum yield of the product)
A. 2H <sub>2</sub> (1g) + O <sub>2</sub> (1g) → 2H <sub>2</sub> O	(p) 1.125 g
B. 3H <sub>2</sub> (1g) + N (1g) → 2NH <sub>3</sub>	(q) 1.028 g
C. H <sub>2</sub> (1g) + Cl <sub>2</sub> (1g) → 2HCl	(r) 1.214 g
D. 2H <sub>2</sub> (1g) + C (1g) → CH <sub>4</sub>	(s) 1.333 g

**149.** Match the following:

List I	List II
A. NH <sub>3</sub> → NO <sub>3</sub> <sup>-</sup>	(p) M/5
B. Fe <sub>2</sub> S <sub>3</sub> → 2FeSO <sub>4</sub> + SO <sub>2</sub>	(q) M
C. KMnO <sub>4</sub> H <sup>+</sup> MnSO <sub>4</sub>	(r) M/20
D. CuS → CuSO <sub>4</sub>	(s) M/8

**150.** Match the stoichiometric coefficients in List I with the species in List II and involved in the balanced equation of the following reaction:



List I	List II
A. FeC <sub>2</sub> O <sub>4</sub>	(p) 3
B. MnO <sub>4</sub> <sup>-</sup>	(q) 5
C. H <sup>+</sup>	(r) 10
D. CO <sub>2</sub>	(s) 24

**151.** Match the following:

- | <b>List I</b>                                                                                                                                                                                                                               | <b>List II</b> |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|
| A. A 0.5 g sample of dichromate ore required 20 ml of 0.22 M ferrous ammonium sulphate for complete reduction. What is the percentage of chromium in the sample?                                                                            | (p) 29.4       |
| B. A sample was analysed and reported to contain 21 % NaOH. Later it was found that the basic material is KOH rather than NaOH. What is the percentage of KOH in the sample?                                                                | (q) 20.6       |
| C. 25 ml of H <sub>2</sub> O <sub>2</sub> solution when added to excess acidified KI solution, evolves iodine, which require 20 ml of 0.3125 N sodium thiosulphate solution. What is the volume strength of H <sub>2</sub> O <sub>2</sub> ? | (r) 1.4        |
| D. 0.5 g of fuming H <sub>2</sub> SO <sub>4</sub> (oleum) is diluted with water. This solution is completed neutralized by 26.7 ml of 0.4 N NaOH. What is the percentage of free SO <sub>3</sub> in the sample?                             | (s) 15.25      |

**152.** Match the following:

- | <b>List I</b>                                                              | <b>List II</b>                              |
|----------------------------------------------------------------------------|---------------------------------------------|
| A. Change of NO to NO <sub>3</sub> <sup>-</sup>                            | (p) Oxidation number changes from +7 to +2  |
| B. Change of P <sub>4</sub> to H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> | (q) Oxidation number changes +6 to +3       |
| C. KMnO <sub>4</sub> in acidic medium                                      | (r) Oxidation number changes from 0 to +1   |
| D. K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> in acidic medium          | (s) Oxidation number changes from +2 to +5. |

**153.** Match the following:

- | <b>Column I</b> | <b>Column II</b>                       |
|-----------------|----------------------------------------|
| A. 5.55 mole    | (p) 4.48 L of SO <sub>2</sub> at N.T.P |
| B. 0.1 mole     | (q) 100 mL H <sub>2</sub> O            |

## 1.46 ■ Mole Concept and Stoichiometry

- C. 0.2 mole (r) 22 gm  $\text{CO}_2$   
 D. 0.5 mole (s) 2.24 L  $\text{NH}_3$   
                  (t) 0.1 gm atom of Fe

**154.** Match the following:

**List I** ( $1D = 10^{-18}$  esu cm,  $1D = 3.33 \times 10^{-30}$  cm)      **List II** (Electronic charge =  $4.8 \times 10^{-10}$  esu)

- A. A diatomic molecule has a dipole moment equal to 1.2 D. If bond length is 1.0 Å. What fraction (%) of electronic charge exists on each atom. (p) 40 %

B. The dipole moment of LiH is  $1.94 \times 10^{-29}$  cm and intermolecular distance between Li and H in this molecule is 1.596 Å. What is percent ionic character in molecule. (q) 60 %

C. One litre of mixture of CO and  $\text{CO}_2$  is passed through red hot charcoal in tube. The new volume becomes 1.4 litre. Find out % composition of CO at same P and T. (r) 76 %

D. Given sample of oleum is labeled as 109 %. Calculate the % of free  $\text{SO}_3$  in it. (s) 25 %

**155.** Match the following:

<b>List I</b>	<b>List II</b>
A. 10 ‘vol’ H <sub>2</sub> O <sub>2</sub>	(p) 0.0
B. 11.2 ‘vol’ H <sub>2</sub> O <sub>2</sub>	(q) 0.5
C. 5.6 ‘vol’ H <sub>2</sub> O <sub>2</sub>	(r) 3.0
D. 20 ‘vol’ H <sub>2</sub> O <sub>2</sub>	(s) 2N

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- 156.** The number of moles of  $\text{KMnO}_4$  that will be needed to react completely with one mole of ferrous oxalate in acidic solution is



[IIT 1997]

- 157.** The normality of 0.3 M phosphorous acid ( $H_3PO_3$ ) is



[IIT 1999]

- 158.** An aqueous solution of 6.3 g of oxalic acid dihydrate is made upto 250 mL. The volume of 0.1 N NaOH required to completely neutralizes 10 mL of this solution is

- a.** 40 mL                            **b.** 20 mL  
**c.** 10 mL                            **d.** 4 mL

[HT 2001]

- 159.** In the standardization of  $\text{Na}_2\text{S}_2\text{O}_3$  using  $\text{K}_2\text{Cr}_2\text{O}_7$  by iodometry, the equivalent weight of  $\text{K}_2\text{Cr}_2\text{O}_7$  is

  - a. same as molecular weight
  - b. molecular weight/2
  - c. molecular weight/4
  - d. molecular weight/6

[IIT 2001]

- 160.** How many moles of electrons weigh one kilogram?

(mass of electron =  $9.108 \times 10^{-31}$  kg, Avogadro number =  $6.023 \times 10^{23}$ )

- a.  $6.023 \times 10^{23}$

b.  $1/9.108 \times 10^{31}$

- c.  $\frac{6.023}{9.08} \times 10^{54}$

d.  $\frac{1}{9.108 \times 6.023} \times 10^6$

[IIT 2002]

- 161.** Which has maximum number of atoms?

- a. 24 g of C (12)
  - b. 56 g of Fe (56)
  - c. 27 g of Al (27)
  - d. 108 g of Ag (108)

[IIT 2003]

- 162.** Mixture X = 0.02 mol of  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  was prepared in 2 litre of solution.

1 litre of mixture X + excess  $\text{AgNO}_3 \rightarrow \text{Y}$ .

I litre of mixture X + excess  $\text{BaCl}_2 \rightarrow \text{Z}$ .

Number of moles of Y and Z are

- |               |               |
|---------------|---------------|
| a. 0.02, 0.01 | b. 0.01, 0.01 |
| c. 0.01, 0.02 | d. 0.02, 0.02 |

[IIT 2003]

163. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenyl amine as indicator. The number of moles of Mohr's salt required per mole of dichromate is

- |      |      |
|------|------|
| a. 3 | b. 4 |
| c. 5 | d. 6 |

[IIT 2007]

164. Given that the abundances of isotopes  $^{54}\text{Fe}$ ,  $^{56}\text{Fe}$  and  $^{57}\text{Fe}$  are 5%, 90% and 5% respectively, the atomic mass of Fe is

- |          |          |
|----------|----------|
| a. 55.85 | b. 55.95 |
| c. 55.75 | d. 56.05 |

[IIT 2009]

## ANSWERS

### Straight Objective Type Questions

- |       |       |       |       |       |       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1. a  | 2. c  | 3. c  | 4. b  | 5. a  | 6. b  | 7. d  | 8. d  | 9. b  | 10. c | 11. b | 12. d |
| 13. b | 14. a | 15. c | 16. a | 17. c | 18. c | 19. b | 20. c | 21. c | 22. d | 23. a | 24. d |
| 25. d | 26. d | 27. c | 28. a | 29. b | 30. d | 31. a | 32. b | 33. c | 34. b | 35. d | 36. c |
| 37. d | 38. c | 39. c | 40. b | 41. b | 42. a | 43. c | 44. b | 45. b | 46. b | 47. c | 48. b |
| 49. c | 50. d | 51. a | 52. a | 53. a | 54. a | 55. a | 56. c | 57. b | 58. a | 59. b | 60. d |
| 61. b | 62. a | 63. c | 64. d | 65. b |       |       |       |       |       |       |       |

### Brainteasers Objective Type Questions

- |       |       |       |       |       |       |       |       |       |       |        |       |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|-------|
| 66. d | 67. b | 68. a | 69. c | 70. a | 71. d | 72. d | 73. c | 74. d | 75. b | 76. c  | 77. a |
| 78. a | 79. b | 80. d | 81. c | 82. d | 83. c | 84. b | 85. a | 86. c | 87. c | 88. c  | 89. c |
| 90. a | 91. c | 92. b | 93. b | 94. b | 95. d | 96. a | 97. b | 98. b | 99. a | 100. c |       |

### Multiple Correct Answer Type Questions

- |            |           |            |            |           |            |           |            |
|------------|-----------|------------|------------|-----------|------------|-----------|------------|
| 101. b,c,d | 102. b, d | 103. a, b  | 104. b,c,d | 105. a, d | 106. a,c   | 107. a, b | 108. a,c,d |
| 109. a, b  | 110. c, d | 111. a,c,d | 112. a,c,d | 113. c, d | 114. b,c,d | 115. c, d | 116. a, c  |

### Linked-Comprehension Type Questions

#### Comprehension 1

- |        |        |        |
|--------|--------|--------|
| 117. b | 118. d | 119. d |
|--------|--------|--------|

#### Comprehension 2

- |        |        |        |        |
|--------|--------|--------|--------|
| 120. b | 121. c | 122. c | 123. b |
|--------|--------|--------|--------|

#### Comprehension 3

- |        |        |        |        |
|--------|--------|--------|--------|
| 124. a | 125. b | 126. b | 127. b |
|--------|--------|--------|--------|

#### Comprehension 4

- |        |        |        |
|--------|--------|--------|
| 128. b | 129. c | 130. d |
|--------|--------|--------|

#### Assertion Reason Type Questions

- |        |        |        |        |
|--------|--------|--------|--------|
| 131. b | 132. e | 133. e | 134. b |
| 135. a | 136. a | 137. c | 138. b |
| 139. a | 140. a | 141. a | 142. a |
| 143. a | 144. a | 145. a | 146. d |

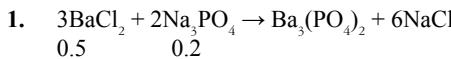
**Matrix-Match Type Questions**

147. A - (q, r), B - (q), C - (p, s), D - (p, s)  
 149. A-(s), B-(r), C-(p), D-(s)  
 151. A-(s), B-(p), C-(r), D-(q)  
 153. A - (q), B - (s, t), C - (p), D - (r)  
 155. A-(r), B-(s), C-(q), D-(p)

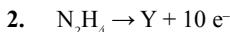
148. A-(p), B-(r), C-(q), D-(s)  
 150. A-(q), B-(p), C-(s), D-(r)  
 152. A-(s), B-(r), C-(p), D-(q)  
 154. A-(s), B-(r), C-(p), D-(q)

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156. c      157. c      158. a      159. d      160. d      161. a      162. b      163. d      164. b

**Hints and Explanations****Straight Objective Type Questions**

Limiting reagent is  $\text{Na}_2\text{PO}_4$  (0.2 mol), which gives 0.1 mol of  $\text{Ba}_3(\text{PO}_4)_2$ .



Oxidation state of N in  $\text{N}_2\text{H}_4$ :

$$2X + 4 = 0$$

$$X = -2$$

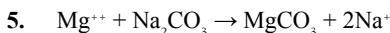
The two, nitrogen atoms will balance the charge of  $10 \text{ e}^-$ .

So oxidation state of N will increase by +5, that is, from -2 to +3.

3. Eq. mass =  $\frac{\text{molecular weight}}{\text{Change in oxidation no. of Mn}}$   
 $= \frac{\text{mol. wt.}}{4 - 2} = \frac{\text{mol. wt.}}{2}$

(oxidation number of Mn in  $\text{MnSO}_4$  = +2 and Mn in  $\text{MnO}_2$  = +4)

4. Molality of a solution remains independent of temperature.



$$1 \text{ g eq. } 1 \text{ g eq.}$$

$1 \text{ g eq. of Mg}^{2+} = 12 \text{ g of Mg}^{2+} = 12000 \text{ mg} = 1000 \text{ milli eq. of Na}_2\text{CO}_3$

Hence  $12 \text{ mg Mg}^{2+} = 1 \text{ milli eq. Na}_2\text{CO}_3$

6. As 1 mol  $\text{CCl}_4$  vapour =  $12 + 4 \times 35.5$   
 $= 154 \text{ g} \equiv 22.4 \text{ L at STP}$   
 $\text{So density} = \frac{W}{V} = \frac{154}{22.4} \text{ g L}^{-1}$   
 $= 6.875 \text{ g L}^{-1}$

7.  $22400 \text{ cc} = 6.02 \times 10^{23} \text{ molecules}$   
 $1 \text{ cc } \text{N}_2\text{O} = \frac{6.02 \times 10^{23}}{22400} \text{ molecules}$   
 $= \frac{3 \times 6.02 \times 10^{23}}{22400} \text{ atoms}$   
 $= \frac{1.8}{224} \times 10^{22} \text{ atoms}$

number of electrons in a molecule of  $\text{N}_2\text{O} = 7 + 7 + 8 = 22$

hence number of electrons  
 $= \frac{6.02 \times 10^{23}}{22400} \times 22 \text{ electrons}$

8. As normality of 10 volume of  $\text{H}_2\text{O}_2$  = 1.78 N  
 So volume strength of 1.78 N solution = 10  
 Volume strength of 1.5 N  $\text{H}_2\text{O}_2$   
 $= 1.5 \times \frac{10}{1.78} = 8.4$

9. Number of oxygen atoms = number of CO molecules =  $6.022 \times 10^{24}$   
 Number of oxygen molecule  
 $= \frac{1}{2} \times \text{number of oxygen atoms}$

$$= \frac{1}{2} \times 6.022 \times 10^{24} = 3.011 \times 10^{24}$$

number of g molecule of O<sub>2</sub> molecules

$$= \frac{3.011 \times 10^{24}}{6.022 \times 10^{23}} = 5 \text{ g molecule}$$

10. Mol. Mass of CuSO<sub>4</sub>.5H<sub>2</sub>O

$$= 63 + 32 + 16 + 4 + 5 \times 18 = 249$$

6.02 × 10<sup>23</sup> molecules of CuSO<sub>4</sub>.5H<sub>2</sub>O has a mass = 249 g

1 × 10<sup>22</sup> molecules of CuSO<sub>4</sub>.5H<sub>2</sub>O has a

$$\text{mass} = \frac{(249 \text{ g}) \times 1 \times 10^{22}}{6.02 \times 10^{23}} = 4.159 \text{ g}$$

11. Molecular wt of C<sub>60</sub>H<sub>122</sub> = (12 × 60) + 122 = 842

therefore weight of one molecule

$$= \frac{\text{molecular weight of C}_{60}\text{H}_{122}}{\text{Avogadro's number}}$$

$$= \frac{842}{6.023 \times 10^{23}} = 1.4 \times 10^{-21} \text{ g}$$

12. Mol. wt. of ZnSO<sub>4</sub>.7H<sub>2</sub>O

$$= 65 + 32 + (4 \times 16) + 7(2 \times 1 + 16) = 287$$

percentage mass of Zn

$$= \frac{65}{287} \times 100 = 22.65 \%$$

13. Wt. of Mg(HCO<sub>3</sub>)<sub>2</sub> = 7.3 gm.



Mol. wt. of Mg(HCO<sub>3</sub>)<sub>2</sub>

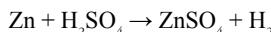
$$= 24 + (1 + 12 + 48) \times 2 = 146 \text{ gm}$$

As 146 gm of Mg(HCO<sub>3</sub>)<sub>2</sub> evolves 22.4 L of CO<sub>2</sub> at STP.

So 7.3 gm of Mg(HCO<sub>3</sub>)<sub>2</sub> evolves

$$\frac{7.3 \times 22.4}{146} = 1.12 \text{ l} = 1120 \text{ ml}$$

14. Atomic weight of Zn = 95 and volume of H<sub>2</sub> = 224 ml



$$\frac{\text{Volume of H}_2}{22400} = \frac{\text{Weight of Zn}}{\text{Atomic weight of Zn.}}$$

$$\text{Wt. of Zn} = \frac{224 \times 65}{22400} = 0.65 \text{ gm}$$

15. Number of moles of NH<sub>3</sub> =  $\frac{\text{mass in gm}}{\text{Mol. mass}}$

$$= \frac{4.25}{17} = 0.25 \text{ mole}$$

$$\text{Number of atoms} = 0.25 \times 6 \times 10^{23}$$

$$= 1.50 \times 10^{23} \text{ atoms}$$

16. Mol. wt. of ammonia = 14 + (3 × 1) = 17.

As wt. of ammonia = 4.25 gm

So 17 gm of ammonia contains 6.02 × 10<sup>23</sup> atoms

4.25 gm of ammonia contain

$$= \frac{6.02 \times 10^{23} \times 4.25}{17} = 1.5 \times 10^{23}.$$

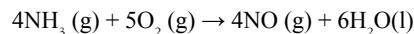
17. Atomic wt. of oxygen = 16 gm

Wt. of 6.02 × 10<sup>23</sup> atoms of oxygen is 16 gm

$$\text{So weight of 1 atom} = \frac{16}{6.02 \times 10^{23}}.$$

$$= 2.656 \times 10^{-23} \text{ gm}$$

18. According to stoichiometry they should react as follows:



4 moles	5 moles	4 moles	6 moles
0.8 moles	1 mole	0.8 mole	1.2 moles

Thus for 1 mole O<sub>2</sub> only 0.8 mole of NH<sub>3</sub> is consumed. So O<sub>2</sub> is consumed completely.

19. Mol. wt. of H<sub>3</sub>PO<sub>4</sub> is 98 and change in its valence = 1.

$$\text{Eq. wt. of H}_3\text{PO}_4 = \frac{\text{mol. wt.}}{\text{Change in valency}}. \\ = 98/1 = 98.$$

20. BaCO<sub>3</sub> → BaO + CO<sub>2</sub>

$$197 \text{ gm}$$

197 gm of BaCO<sub>3</sub> released CO<sub>2</sub> = 22.4 litre

$$1 \text{ gm of BaCO}_3 \text{ released CO}_2 = \frac{22.4}{197} \text{ litre}$$

9.85 gm of BaCO<sub>3</sub> released CO<sub>2</sub>

$$= \frac{22.4}{197} \times 9.85 = 1.12 \text{ litre}$$

21. Na<sub>2</sub>CO<sub>3</sub> + 2HCl → 2NaCl + H<sub>2</sub>O + CO<sub>2</sub>

106 gm gives 22.4 lit

## 1.50 ■ Mole Concept and Stoichiometry

$$2.12 \text{ gm gives } \frac{2.12 \times 22.4}{106} = \frac{22.4}{50}$$

$$= 0.448 \text{ litre.}$$

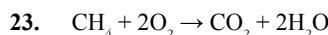
22. Suppose the mol. wt. of enzyme = x

So in 100 g of enzyme wt. of Se = 0.5 gm

$$\text{In } x \text{ g of enzyme wt. of Se} = \frac{0.5}{100} \cdot x$$

$$\text{hence } 78.4 = \frac{0.5 \cdot x}{100}$$

$$x = 15680 = 1.568 \times 10^4$$



$$16 \text{ g} \quad 2 \times 22.4$$

$$32 \text{ g} \quad 2 \times 22.4 \times 32 \quad = 4 \times 22.4 \\ 16$$

$$= 89.6 \text{ litre of O}_2.$$

24. Volume of one drop of water = 0.0018 ml.

As the density of water is 18 g/cc,

So 18 ml of water = 1 mole of water =  $6.02 \times 10^{23}$  molecules of water.

Thus 0.0018 ml of water =  $18 \times 10^{-4}$  gm of water molecules of water

$$= (0.023 \times 10^{23}) \times 10^{-4}$$

$$= 6.023 \times 10^{19} \text{ molecules.}$$

25. As molecular weight of  $\text{C}_{60}\text{H}_{122}$

$$= (12 \times 60) + 122 = 842.$$

So weight of one molecule

$$= \frac{\text{mol. wt. of C}_{60}\text{H}_{12}}{\text{Avogadro's number}} = \frac{842}{6.023 \times 10^{23}}$$

$$= 1.4 \times 10^{-21} \text{ g}$$

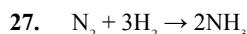
26.  $\frac{\text{Mass of metal oxide}}{\text{Mass of metal chloride}}$

$$= \frac{\text{Eq. mass of metal} + \text{Eq. mass of oxide}}{\text{Eq. mass of metal} + \text{Eq. mass of chloride}}$$

$$= \frac{3}{5} = \frac{E + 8}{E + 35.5}.$$

On solving, we get

$$E = 33.25$$



$$1 \text{ vol} \quad 3 \text{ vol} \quad 2 \text{ vol}$$

$$10 \text{ lit} \quad 30 \text{ lit} \quad 20 \text{ lit}$$

now 10 litre of  $\text{NH}_3$  is formed

$$\text{N}_2 \text{ used} = 5 \text{ liters, left} = 30 - 5 = 25 \text{ lit}$$

$$\text{H}_2 \text{ used} = 15 \text{ liters, left} = 30 - 15 = 15 \text{ lit}$$

28. Let molarity of  $\text{Ba}(\text{OH})_2 = M_1$

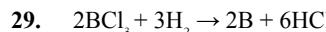
$$\text{Normality} = 2M_1$$

$$\text{Molarity of HCl} = 0.1 \text{ M} = 0.1 \text{ N}$$

$$N_1 V_1 = N_2 V_2$$

$$2M_1 \times 25 = 0.1 \times 35$$

$$M_1 = 0.07 \text{ M}$$



$$2 \text{ mol} \quad 3 \text{ mol} \quad 2 \text{ mol} \\ 21.6 \text{ g} = 2 \text{ mol}$$

$$21.6 \text{ g B} = 2 \text{ mol B} \cong 3 \text{ mol H}_2$$

$$\text{As PV} = nRT$$

$$\text{So V} = \frac{nRT}{P} = \frac{3 \times 0.0821 \times 273}{1} = 67.2 \text{ L}$$

30. 1 g atom of Fe (56 g Fe) is present in 1 mole of the compound

As 4.6 g Fe are present in 100 g of the compound

So 56 g Fe will be present in

$$= \frac{100}{4.6} \times 56 \text{ g}$$

= 1217 g of the compound.

So approximate molecular mass = 1200.

31. Number of molecules in different cases

$$\text{a. } \frac{15}{22.4} \times 6.023 \times 10^{23}$$

$$\text{b. } \frac{5}{22.4} \times 6.023 \times 10^{23}$$

$$\text{c. } \frac{0.5}{2} \times 6.023 \times 10^{23}$$

$$\text{d. } \frac{10}{32} \times 6.023 \times 10^{23}$$

Thus 15 L of  $\text{H}_2$  gas at STP will have maximum number of molecules.

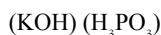
32.  $\text{H}_3\text{PO}_3$  is a dibasic acid (containing two ionizable protons attached to O directly)



$$0.1 \text{ M H}_3\text{PO}_3 = 0.2 \text{ N H}_3\text{PO}_3$$

$$0.1 \text{ M KOH} = 0.1 \text{ N KOH}$$

$$\text{N}_1\text{V}_1 = \text{N}_2\text{V}_2$$



$$1.1 \text{ V}_1 = 0.2 \times 20$$

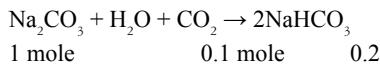
$$\text{V}_1 = 40 \text{ mL}$$

33.  $\text{N}_A = 6.02 \times 10^{23} = 1 \text{ mol}$

$6.02 \times 10^{20}$  molecules = 0.001 mol in 100 ml (0.1 L) solution

$$\text{so molar concentration} = \frac{\text{vol}}{\text{volume in L}} \\ = \frac{0.001}{0.1} = 0.01 \text{ M}$$

34. 10 g that is, 0.1 mole  $\text{CaCO}_3$  is decomposed to 0.1 mole  $\text{CO}_2$  and 0.1 mole  $\text{CaO}$ .



Because here limiting reagent is  $\text{CO}_2$ .  $\text{NaHCO}_3$  is always twice the number of moles of  $\text{CO}_2$ .

Element	Carbon	Hydrogen
% Composition	92.3	7.7
Atomic ratio	92.3/12	7.7/1
	= 7.69	= 7.7
Simple ratio	7.69/7.69	7.7/7.69
	= 1	= 1

So empirical formula is 'CH'

36. Given:

$$\text{As Cu} = 4 \text{ g}, \text{CuO} = 5 \text{ g}$$

$$\text{So oxygen} = 1 \text{ g}$$

As 1 g of oxygen combines with Cu = 4 g

So 8 g of oxygen combine with Cu =  $4 \times 8 = 32 \text{ g}$

Thus, equivalent weight of Cu = 32.

37. As equal volumes contains equal number of moles

So molar ratio of He :  $\text{CH}_4 = 1 : 1$

Ratio by weight = 4 : 16 = 1 : 4

Thus,  $\text{CH}_4$  present by weight

$$= 4/5 \times 100 = 80 \%$$

38. 1 drop of water =  $\frac{1}{20} \text{ ml} = \frac{1}{20} \text{ g}$

(as  $\text{dH}_2\text{O} = 1 \text{ g ml}^{-1}$ )

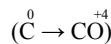
18 g of water = 'A' molecules

$$\frac{1}{20} \text{ g water} = \frac{\text{A}}{18} \times \frac{1}{20}$$

= 0.05 A/18 molecules

39. Eq. wt. of Al = 27/3 = 9

Eq. of wt. of C = 12/4 = 3



$$\text{no. of gm eq. of Al} = \frac{270 \times 10^3}{9} = 30 \times 10^3$$

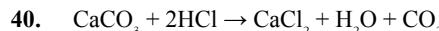
hence no. of gm eq. of C =  $30 \times 10^3$

again,

$$\text{number of gm eq. of C} = \frac{\text{mass in gram}}{\text{gram equivalent wt.}}$$

$$30 \times 10^3 = \frac{\text{mass}}{3 \text{ gm}}$$

$$\text{mass} = 90 \times 10^3 \text{ g} = 90 \text{ kg}$$



100 g	2(36.5)	44 g
	= 73 g	

1 L of 1 N HCl contains 1 g eq. of HCl, as HCl is the limiting agent.

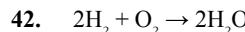
As 73 g HCl liberate  $\text{CO}_2 = 44 \text{ g}$

So 36.5 g HCl will liberate  $\text{CO}_2 = 22 \text{ g}$ .

41. Assume one molecule of the alkaloid contains 'X' N-atoms.

$$\text{Then \% of N} = \frac{14X}{162} \times 100 = 17.28$$

$$\text{Thus, } X = 2.$$



$$2 \text{ ml} \quad 1 \text{ ml}$$

As 2 ml of  $\text{H}_2$  react with 1 ml of  $\text{O}_2$ ,

So 30 ml of  $\text{H}_2$  will react with 15 ml of  $\text{O}_2$

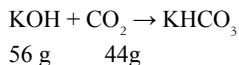
Thus,  $\text{O}_2$  left =  $20 - 15 = 5 \text{ ml}$ .

## 1.52 ■ Mole Concept and Stoichiometry

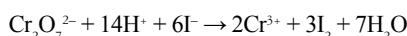
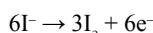
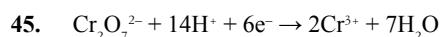
43.  $m = \frac{\text{moles of CH}_3\text{COOH}}{\text{wt. of solvent in kg}} = \frac{2.05 \times 1000}{897}$   
 $= 2.285$

wt. of solvent = wt. of solution – wt. of solute  
 $= [1000 \times 1.02 - 20.5 \times 60] = 897 \text{ g}$

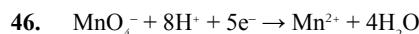
44. Weight of 11.2 dm<sup>3</sup> of CO<sub>2</sub> gas at STP is 44/2 = 22 g



KOH required for complete neutralization of 22 g  
 $\text{CO}_2 = \frac{56}{44} \times 22 = 28 \text{ g}$



One mole of acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> on reaction with excess KI will liberate 3 moles of I<sub>2</sub>.



Equivalent weight of KMnO<sub>4</sub> in acidic medium

$= \frac{\text{molecular weight}}{5}$   
 $= \frac{158}{5} = 31.6$



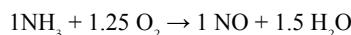
$\text{V}_1/\text{n}_1 = \text{V}_2/\text{n}_2$

$\frac{500}{1} = \frac{100}{\text{n}_2}$

$\text{n}_2 = 1/5$

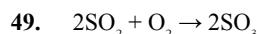
As 1 mole of CO<sub>2</sub> contains  $6.0 \times 10^{23}$  molecules.

So 1/5 mole of CO<sub>2</sub> contains  $1.2 \times 10^{23}$  molecules.



Hence 1 mole of NH<sub>3</sub> reacts with 1.25 moles of O<sub>2</sub> to produce 1 mole of NO and 1.5 moles of H<sub>2</sub>O.

When one mole of ammonia and one mole of oxygen are made to react to completion, then all the oxygen is consumed.



Initial moles	4	4	0
At eq.	4 – 2	$4 - \frac{25}{100} \times 4$	2
	= 2	= 3	= 2 moles
Total number of moles at all gases at equilibrium			
$= 2 + 3 + 2 = 7.$			

50.  $\frac{\text{Weight of metal hydroxide}}{\text{Weight of metal oxide}} = \frac{\text{Equivalent weight of metal hydroxide}}{\text{Equivalent weight of metal oxide}}$

$\frac{1.520}{0.995} = \frac{E_m + 17}{E_m + 8}$

(here E<sub>m</sub> = Equivalent weight of metal)

$1.528 = \frac{E_m + 17}{E_m + 8}$

$0.528 E_m = 4.78$

On solving, we get E<sub>m</sub> = 9.

51. Molarity =  $\frac{\text{Mole of solute}}{\text{Volume of solution in litre}}$

$= \frac{\text{Weight of solute}}{\text{Mol. wt. of solute} \times \text{V in litre}}$

$= \frac{\text{Weight of solute} \times 1000}{\text{Mol. wt. of solute} \times \text{V in ml}}$

$= \frac{2.5 \times 1000}{58.5 \times 100} = 0.427$

52.  $\frac{2E + 410}{195} = \frac{\text{Mass of platinum salt}}{\text{Mass of platinum}}$

$= \frac{0.532}{0.195}$

$E = 61$

Number of nitrogen atoms per molecule of base

$= \frac{244}{61} = 4$

53. As N<sub>1</sub>V<sub>1</sub> = N<sub>2</sub>V<sub>2</sub>

$\frac{490}{49} \times 1 = N_2 \times 10$

$N_2 = \frac{490}{49 \times 10} = 1 \text{ N}$

54.  $\bar{A} = \sum f_i A_i$

(Here  $f_i$  = Fractional abundance,  $A_i$  = Atomic mass)

$$= 0.90 \times 200 + 0.08 \times 199 + 0.02 \times 202$$

$$= 180 + 15.92 + 4.04$$

$$\approx 200 \text{ amu}$$

55. 44.1 g of anhydrous  $\text{Na}_2\text{SO}_4$  are associated with  $\text{H}_2\text{O} = 55.9 \text{ g}$

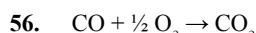
Molar mass of anhydrous  $\text{Na}_2\text{SO}_4$

$$= 2 \times 23 + 32 + 4 \times 16 = 142 \text{ g}$$

So 142 g of anhydrous  $\text{Na}_2\text{SO}_4$  will be associated with  $\text{H}_2\text{O}$

$$= \frac{55.9}{44.1} \times 142 \text{ g} = 180 \text{ g}$$

$$= 10 \text{ moles of H}_2\text{O}$$



As 1 L of CO reacts with  $\frac{1}{2}$  L of  $\text{O}_2$  to produce 1 L of  $\text{CO}_2$ . So 10 L  $\text{O}_2$  will react with 20 L of CO to produce 20 L of  $\text{CO}_2$

Thus, CO left = 10 L and  $\text{CO}_2$  produced = 20 L,  $\text{O}_2$  left = 0 L

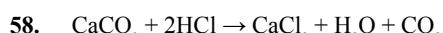
57. As  $40 \text{ cm}^3$  of 0.125 N NaOH neutralize acid = 0.3 g

So  $1000 \text{ cm}^3$  of 1 N NaOH will neutralize acid

$$= \frac{0.3}{40} \times \frac{1000}{0.125} \text{ g} = 60 \text{ g}$$

$1000 \text{ cm}^3$  of 1 N NaOH contain one gram equivalent of NaOH. It will neutralize one gram equivalent of the acid.

Thus, equivalent weight of acid = 60

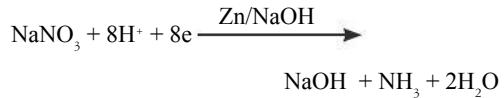


$$100 \text{ g} \quad 2(36.5) \\ = 73 \text{ g}$$

So 5 g  $\text{CaCO}_3$  will completely react with HCl

$$= \frac{73}{100} \times 5 = 3.65 \text{ g}$$

59. Ammonia is formed by reduction of nitrates and nitrites with Zn and NaOH. Zn and caustic soda produce nascent hydrogen which reacts with nitrates to form ammonia.



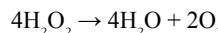
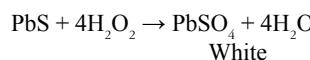
From the equation –

Mass of 8 moles of electron absorbs 85 g  $\text{NaNO}_3$

As Mass of 1 mole of electron absorbs

$$\frac{85}{8} = 10.65 \text{ g of } \text{NaNO}_3,$$

60. When blackened statues are treated with  $\text{H}_2\text{O}_2$ , the  $\text{PbS}$  is oxidized to  $\text{PbSO}_4$ , which is colourless (White)



$$4(2 + 32) \quad 2 \times 22.4 \text{ litre} \\ = 136 \text{ g} \quad \text{at N.T.P.}$$

From the above equation, we can derive that –

In transferring 1 mole of PbS to  $\text{PbSO}_4$ , the volume of '10 volume' of  $\text{H}_2\text{O}_2$  required is 44.8 time at NTP.

61. Let the oxide of unknown element be  $MO$ .

Given that oxygen content is 20% by weight.

Then

$$\text{Eq. weight of unknown element (M)} = \frac{80}{20 \times 8 \text{ g}}$$

$$\text{Equivalent weight of unknown element (M)} = 32 \text{ g.}$$

62. From the reaction

$$\frac{\text{Normality}}{\text{Molarity}} = \frac{\text{Molecular mass}}{\text{Equivalent mass}} = n$$

For 2 N HCl

$$\text{Molarity} = \frac{\text{Normality} \times \text{Equivalent weight}}{\text{Molecular weight}}$$

$$\text{Molarity} = \frac{2 \times 36.5}{36.5} = 2$$

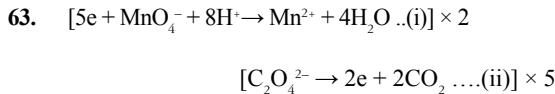
For 4 N  $\text{H}_2\text{SO}_4$

$$\text{Molarity} = \frac{\text{Normality} \times \text{Equivalent weight}}{\text{Molecular weight}}$$

$$\text{Molarity} = \frac{4 \times 49}{98} = 2$$

## 1.54 ■ Mole Concept and Stoichiometry

Hence 4 N  $\text{H}_2\text{SO}_4$  and 2 N HCl solution will have same alcohol and nitrogen is evolved.



As 2 moles of  $\text{MnO}_4^-$  required to oxidize 5 moles of oxalate

So number of moles of  $\text{MnO}_4^-$  required to oxidize 1 mole of oxalate =  $2/5 = 0.4$

65. Molarity (M) =  $\frac{300/100}{10^6/10^3} = \frac{3}{10^3} = 0.003 \text{ M}$

### Brainteasers Objective Type Questions

66. Specific volume (vol of 1 gm) cylindrical virus particle =  $6.02 \times 10^{-2} \text{ cc/gm}$

$$\text{Radius of virus (r)} = 7 \text{ \AA} = 7 \times 10^{-8} \text{ cm}$$

$$\text{Length of virus} = 10 \times 10^{-8} \text{ cm}$$

$$\text{Volume of virus } \pi r^2 l = \frac{22}{7} \times (7 \times 10^{-8})^2 \times 10 \times 10^{-8}$$

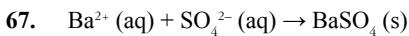
$$= 154 \times 10^{-23} \text{ cc}$$

$$\text{wt. of one virus particle} = \frac{\text{volume}}{\text{specific volume}}$$

$$\text{mol. wt. of virus} = \text{wt. of N}_A \text{ particle}$$

$$= \frac{154 \times 10^{-23}}{6.02} \times 10^{-2} \times 6.02 \times 10^{23}$$

$$= 15400 \text{ g/mol} = 15.4 \text{ kg/mole}$$



$$0.4123 \text{ g} \quad \text{BaSO}_4 \times \frac{137.3 \text{ g Ba}}{233.4 \text{ g BaSO}_4}$$

$$= 0.2425 \text{ g Ba}$$

$$\text{Mass \%} = \frac{\text{g Ba}}{\text{g sample}} \times 100$$

$$= \frac{0.2425 \text{ g Ba}}{6.977 \text{ g sample}} \times 100$$

$$= 3.476 \% \text{ Ba}$$

68. Weight of  $6.023 \times 10^{23}$  molecule of water = 18 g

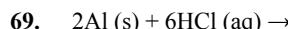
As volume occupied by  $6.023 \times 10^{23}$  molecule of water (density =  $1 \text{ g cm}^{-3}$ ) will be

$$= \frac{18 \text{ g}}{1 \text{ g cm}^{-3}} = 18 \text{ cm}^3 \text{ or ml}$$

So volume occupied by one molecule of water

$$= \frac{18}{6.023 \times 10^{23}} = 2.988 \times 10^{-23}$$

$$= 3.0 \times 10^{-23} \text{ cm}^3$$



As 6 moles of HCl evolved  $\text{H}_2$  at STP

$$= 3 \times 22.4 \text{ L}$$

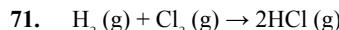
So 1 mole of HCl will evolve  $\text{H}_2$  at STP

$$= \frac{3 \times 22.4}{6} = 11.2 \text{ L}$$

70. Suppose X g of  $\text{Ca(OH)}_2$  will be dissolved X g  $\text{Ca(OH)}_2$

$$= 250.0 \text{ ml sol.} \times (1 \text{ L sol./1000 ml sol.}) \times (0.0200 \text{ mol Ca(OH)}_2/\text{1 L sol.}) \times [74.10 \text{ g Ca(OH)}_2/\text{1 L sol.}]$$

On solving we get, = 0.370 g  $\text{Ca(OH)}_2$

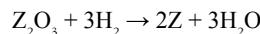


$$\begin{array}{ccc} 1 \text{ mole} & 1 \text{ mole} & 2 \text{ mole} \\ 22.4 \text{ L} & 22.4 \text{ L} & 2 \times 36.5 \text{ g} \end{array}$$

For the formation of 3.65 g HCl,  $\text{H}_2$  or  $\text{Cl}_2$  required

$$= \frac{22.4}{2 \times 36.5} \times 3.65 \text{ L} = 1.12 \text{ L}$$

72. Valency of metal in  $\text{Z}_2\text{O}_3 = 3$



$$0.1596 \text{ g of Z}_2\text{O}_3 \text{ react with H}_2 = 6 \text{ mg} = 0.006 \text{ g}$$

1 g of  $\text{H}_2$  react with

$$= \frac{0.1596}{0.006} = 26.6 \text{ g of Z}_2\text{O}_3$$

$$\text{Eq. Wt. of Z}_2\text{O}_3 = 26.6$$

$$\text{Eq. wt. of Z} + \text{Eq. wt of O} = E + 8 = 26.6$$

$$\text{Eq. wt. of Z} = 26.6 - 8 = 18.6$$

$$\text{Atomic wt. of Z} = 18.6 \times 3 = 55.8$$

73. Wt. of  $\text{MSO}_4 = 1.375 \times \frac{148}{233} = 0.8734 \text{ g}$   
 Wt. of  $\text{MSO}_4$  in the original solution (61.5 g)  $= 0.8734 \times 10 = 8.734 \text{ g}$   
 Wt. of solvent  $= 61.5 - 8.734 = 52.766 \text{ g}$   
 Wt. of  $\text{MSO}_4$  per 100 g of solvent  
 $= 8.734 \times \frac{100}{52.766} = 16.55 \text{ g}$   
 Solubility of  $\text{MSO}_4$  is 16.55 g per 100 g of solvent.
74.  $2\text{C}_6\text{H}_6(\text{l}) + 15\text{O}_2(\text{g}) \rightarrow 12\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$   
 $2(78) \quad 15(32)$   
 156 gm of benzene required oxygen  $= 15 \times 22.4 \text{ litre}$   
 1 gm of benzene required oxygen  
 $= \frac{15 \times 22.4}{156} \text{ litre}$   
 39 gm of benzene required oxygen  
 $= \frac{15 \times 22.4 \times 39}{156} = 84.0 \text{ litre}$
75. Eq. mass of ferrous ammonium sulphate = 392  
 Normality of the salt solution  
 $= \frac{3.92}{392} \times \frac{1}{100} \times 1000 = 0.1 \text{ N}$   
 20 ml of 0.1 N salt solution = 18 ml of  $\text{KMnO}_4$  solution  
 Normality of  $\text{KMnO}_4$  solution  
 $= \frac{20 \times 0.1}{18} = \frac{1}{9} \text{ N}$   
 Eq. mass of  $\text{KMnO}_4$  = 31.6  
 So strength of  $\text{KMnO}_4$  solution  $= 1/9 \times 31.6 = 3.511 \text{ g L}^{-1}$  approx
76. 1000 ml of 0.02 N oxalic acid has = 0.02 g eq.  
 So 100 ml of 0.02 N oxalic acid has = 0.002 g eq = 0.001 mole  
 $(M = N \times \text{basicity})$   
 Thus number of molecules  
 $= 10^{-3} \times 6.022 \times 10^{23}$   
 $= 6.022 \times 10^{20}$

77. In the absence of  $\text{H}_2\text{O}$ ,  
 $2\text{KO}_2 + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3 + 3/2 \text{ O}_2$   
 $10^{-3} \quad 10^{-3} \text{ mole}$   
 The limiting reagent is  $\text{KO}_2$  in the sense that it limits the amount of  $\text{CO}_2$  consumed.  
 $\text{CO}_2$  consumed  $= 10^{-3}/2 \text{ mole}$   
 $\text{O}_2$  produced  $= \frac{10^{-3}}{2} \times \frac{3}{2} \text{ mole}$   
 $\equiv 22.4 \text{ cm}^3 \times \frac{3}{4} \text{ at STP} = 16.8 \text{ cm}^3 \text{ at STP}$
78. (I) mass of one O atom  $= \frac{16}{6.02 \times 10^{23}} \text{ g}$   
 $= 2.66 \times 10^{-23} \text{ g}$   
 (II) mass of one N atom  $= \frac{14}{6.02 \times 10^{23}} \text{ g}$   
 $= 2.33 \times 10^{-23} \text{ g}$   
 (III) 1 g molecule of oxygen  $= 32 \text{ g } 1 \times 10^{-10} \text{ g}$   
 molecule of oxygen  
 $= 32 \times 10^{-10} = 3.2 \times 10^{-9} \text{ g}$   
 (IV) 1 g atom of copper  $= 63 \text{ g } 1 \times 10^{-7} \text{ g atom of}$   
 copper  
 $= 63 \times 10^{-7} = 6.3 \times 10^{-6} \text{ g}$   
 so the correct order is  
 II < I < III < IV
79.  $\text{PbO} + 2\text{HCl} \rightarrow \text{PbCl}_2 + \text{H}_2\text{O}$   
 $X \text{ mol} \quad 2X \text{ mol} \quad X \text{ mol}$   
 $\frac{6.5}{224} \text{ mol} \quad \frac{3.2}{36.5} \text{ mol}$   
 $= 0.029 = 0.087 \text{ mol}$   
 Thus, 0.029 moles of lead (II) chloride will be formed from a reaction between 6.5 g of PbO and 3.2 g of HCl.
81.  $\text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}$   
 $0.002 \quad 0.01 \quad 0.006$   
 $\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$   
 $\text{Br}_2 \equiv \text{I}_2 \equiv 2\text{Na}_2\text{S}_2\text{O}_3$   
 Amount of  $\text{Na}_2\text{S}_2\text{O}_3$  reacting  $= 0.006 \times 2$   
 $= 0.012 \text{ mole}$

## 1.56 ■ Mole Concept and Stoichiometry

$$= 0.1 \times v \times 10^{-3} \text{ mole},$$

Here 'v' is the volume of  $\text{Na}_2\text{S}_2\text{O}_3$  in ml.

$$v = \frac{0.012 \text{ ml}}{0.1 \times 10^{-3}} = \frac{0.012 \text{ ml}}{10^{-4}} = 120 \text{ ml}$$

82. Suppose the weight of the sample = 100 g

So the number of equivalent of NaOH = 21/40

If the sample, contains KOH instead of NaOH same number of equivalent of KOH should be present in the sample.

$$\text{So weight of KOH} = \frac{21}{40} \times 56 = 29.4$$

83. 100 gm of metal oxide contains 53 g of metal

As Equivalent mass of element

$$= \frac{\text{Mass of element}}{\text{Mass of oxygen}} \times 8 = \frac{53}{47} \times 8 = 9$$

So, Atomic mass = Equivalent mass of an element  $\times$  valency

$$= 9 \times 3 = 27 \text{ gm}$$

84. Equivalents of oxalate present = Equivalents of  $\text{KMnO}_4$  used

$$= 90 \times \frac{1}{20} \times 10^{-3}$$

Mass of oxalate present

$$= \frac{90 \times 1}{20 \times 10^{-3}/2} \times 88 = 0.198 \text{ g}$$

% of oxalate in the given sample

$$= \frac{0.198}{0.3} \times 100 = 66$$

85.  $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$

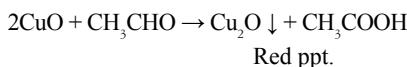
1 vol.	3 vol.	2 vol.	3 vol.
1 mol.	3 mol.	2 mol.	3 mol.

(As vol% = mol%).

One gram mol of any occupies 22.4 litre at NTP.

1 mol of  $\text{Fe}_2\text{O}_3$  requires 3 mol of CO for its reduction that is, 1 mol of  $\text{Fe}_2\text{O}_3$  requires  $3 \times 22.4$  litre or  $67.2 \text{ dm}^3$  CO to get itself reduced.

91. Ethanol does not react with Fehling's reagent, only acetaldehyde reacts as follows:



$$\text{Moles of Cu}_2\text{O} = \frac{1.2}{143}.$$

$$\text{Moles of CH}_3\text{CHO} = \frac{1.2}{143}.$$

$$\text{So \% of acetaldehyde} = \frac{44 \times 1.2}{143 \times 0.5} \times 100$$

$$= 74 \%$$

93. Weight of  $\text{CaCO}_3$  = 5 gm

$$\text{Mole} = \frac{5}{100} = 0.05$$

$$\text{Mole of HCl} = 0.05 \times 2 = 0.1$$

$$\text{Weight} = 0.1 \times 36.5 = 3.65$$

$$\text{Volume of HCl} = \frac{3.65}{1.825} = 2 \text{ ml}$$

$$98. 2 \times \frac{0.7}{106 + 18x} = 5 \times 19.8 \times \frac{1}{10} \times \frac{1}{1000}.$$

On solving, we get

$$x = 2$$

100. Weight of bromine in the bromide

$$= 1.32 \times \frac{80}{188} = 0.562 \text{ g}$$

$$\text{Weight of A} = 0.722 - 0.562 = 0.16 \text{ g}$$

$$\text{Eq. weight of A} = 0.16 \times \frac{80}{0.562} = 22.8$$

$$\text{Valency of A} = \frac{\text{atomic weight}}{\text{Equivalent weight}} \\ = \frac{91.2}{22.8} = 4$$

### Multiple Correct Answer Type Questions

109. Suppose the mole of  $\text{C}_2\text{H}_5\text{OH}$  is  $n_1$  and mole of  $\text{H}_2\text{O}$  is  $n_2$ .

$$\frac{n_1}{n_1 + n_2} = \frac{1}{4}.$$

$$\frac{n_1}{n_2} = \frac{1}{3}.$$

$$\frac{W_1}{W_2} = \frac{n_1 \times M_1}{n_2 \times M_2} = \frac{1}{3} \times \frac{46}{18} = \frac{46}{54}$$

% by weight of  $\text{C}_2\text{H}_5\text{OH}$

$$= \frac{46 \times 100}{46 + 54} = 0.46$$

% by weight of H<sub>2</sub>O

$$= \frac{54}{54 + 46} \times 100 = 0.54$$

111.  $\frac{4 \times A_x}{4A_x + 96} = 0.572$

$$\frac{A_x}{A_x + 24} = 0.572$$

$$A_x = \frac{0.572 \times 24}{(1 - 0.572)}$$

$$A_x = 32$$

116. As 1 mol or 28 gm N<sub>2</sub> reacts with 3 mol or 6 gm H<sub>2</sub>

$$\text{So } 2000 \text{ g of N}_2 \text{ will react with H}_2 = \frac{6}{28} \times 2000 \text{ g} \\ = 428.6 \text{ g}$$

Here N<sub>2</sub> is the limiting reagent while H<sub>2</sub> is the excess reagent

As 1 mol of N<sub>2</sub> produces NH<sub>3</sub> = 2 mol = 34 g

$$\text{So } 2000 \text{ g of N}_2 \text{ will produce NH}_3 = \frac{34}{28} \times 2000 \text{ g} \\ = 2.428 \text{ kg}$$

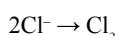
$$\text{Mass left unreacted (for H}_2\text{)} = 1000 - 428.6 \\ = 0.571 \text{ kg H}_2$$

Hence statements a., c. are correct.

### Linked-Comprehension Type Questions

117. NaCl → Na<sup>+</sup> + Cl<sup>-</sup>

At anode:



Moles of Cl<sup>-</sup> = 2 in 500 ml.

Therefore 1 mole of Cl<sub>2</sub> evolves.

118. Na – Hg (amalgam) formed = 2 moles at cathode

119. Moles of electrons (2 Faraday) are required.

$$1F = 96500$$

$$2F = 193000$$

120. H<sub>2</sub>O + SO<sub>3</sub> → H<sub>2</sub>SO<sub>4</sub>;

As 18 g water combines with 80g SO<sub>3</sub>

So 9 g of H<sub>2</sub>O combines with 40 g of SO<sub>3</sub>.

100g of oleum contains 40 g of SO<sub>3</sub>

or 40 % free SO<sub>3</sub>

121. Initial moles of free SO<sub>3</sub> present in oleum

$$= \frac{6}{18} = \frac{1}{3} \text{ moles}$$

= moles of water that can combine with SO<sub>3</sub> moles of free SO<sub>3</sub> combined with water

$$= \frac{4.5}{18} = \frac{1}{4} \text{ mole}$$

moles of free SO<sub>3</sub> remains =  $\frac{1}{3} - \frac{1}{4} = \frac{1}{12}$  mole

$$\text{volume of free SO}_3 \text{ at STP} = \frac{1}{12} \times 22.4$$

$$= 1.792 \text{ L}$$

122. Na<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> → Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O + CO<sub>2</sub>

Moles of CO<sub>2</sub> formed = Moles of Na<sub>2</sub>CO<sub>3</sub>

$$\text{reacted} = \frac{1.06}{106} = 0.01$$

volume of CO<sub>2</sub> formed at 1 atm pressure and 300 K can be given as

$$= \frac{0.01 \times 300 \times 22.4}{273}$$

$$= 0.01 \times 24.615 = 0.24615 \text{ L}$$

123. eq of H<sub>2</sub>SO<sub>4</sub> + eq of SO<sub>3</sub> = eq. of NaOH

$$\frac{x}{98} \times 2 + \frac{(1-x) \times 2}{80} = 27 \times 0.8 \times 10^{-3}$$

On solving x = 0.74

$$\% \text{ of free SO}_3 = \frac{1 - 0.74}{1} \times 100 = 26 \%$$

124. Here 1 L H<sub>2</sub>O<sub>2</sub> gives 16.8 L O<sub>2</sub> at STP

$$\text{Moles of O}_2 = \frac{16.8}{22.4} \\ = 0.75$$

$$\text{Moles of H}_2\text{O}_2 = 0.75 \times 2$$

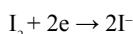
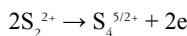
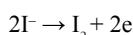
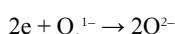
$$= 1.5$$

$$\text{Hence M} = \frac{1.5}{1}$$

$$= 1.5 \text{ M}$$

## 1.58 ■ Mole Concept and Stoichiometry

125. The redox change are



$$\text{Meq. of } H_2O_2 = \text{Meq. of } I_2 = \text{Meq. of } Na_2S_2O_3$$

$$N \times 25 = 0.1 \times 20$$

$$N_{H_2O_2} = 0.08$$

126. m –eq. of  $H_2O_2$  = m –eq. of  $KMnO_4$

$$10 \times N = 0.05 \times 5 \times 40$$

$$\text{So } N = 1$$

$$N = \text{volume strength of } H_2O_2$$

$$5.6$$

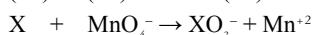
$$\text{volume strength of } H_2O_2 = 5.6 \times 1$$

$$= 5.6$$

127. % (w/V) means how many gm of  $H_2O_2$  is present in 100 mL

As here molarity is 1.5 which means 51 gm  $H_2O_2$  is present in 1 L so 100 mL contents 5.1 gm  $H_2O_2$

128. (+n)      (+7)      (+5)



Changing in ox. no. of  $MnO_4^-$  = 5 (reduction)

$$\text{Eq. wt. of } MnO_4^- = \text{ionic wt.}/5$$

Change in ox. no. of X in  $X^{+n}$  =  $(5-n)$  (oxidation)

$$\text{Eq. wt. of } X^{+n} = (\text{ionic wt.}/5 - n)$$

No. of equivalents of  $MnO_4^-$  in  $1.61 \times 10^{-3}$  moles

$$= 1.61 \times 10^{-3} \times 5$$

No. of equivalents  $X^n$  in  $2.86 \times 10^{-3}$  moles

$$= 2.68 \times 10^{-3} \times (5-n)$$

$$1.61 \times 10^{-3} \times 5 = 2.68 \times 10^{-3} \times (5-n)$$

$$\text{or } 5 - n = \frac{8.05}{2.68}$$

$$\approx 3$$

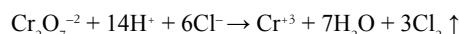
hence  $n = 5 - 3 = 2$  and formula of  $XCl_n$  in  $XCl_2$  Eq.  
wt. of  $XCl_2$  = mole. wt./2

$$= \frac{97 + 71}{2}$$

$$= \frac{168}{2}$$

$$= 84$$

129. The redox equation can be given as



1 mol. of  $Cr_2O_7^{2-}$  ion or  $K_2Cr_2O_7$  oxidises 6  $Cl^-$  ion or 6 equivalents of HCl to 3  $Cl_2$  molecules.

So 40 g  $K_2Cr_2O_7$  will oxidise HCl

$$= \frac{219.0 \times 40}{294}$$

$$= 29.795 \text{ gm.}$$

130. Since for this process n – factor is 15 and not 12

### Assertion-Reason Type Questions

131. Both A and R are true but R is not the correct explanation of A.

According to mole concept, 1 mole of molecules = Gram molecular mass =  $6.023 \times 10^{23}$  molecules

So 58.5 g of NaCl also contains  $6.023 \times 10^{23}$  molecules of NaCl.

132. Both A and R are false. Molar volume (at NTP) = 22.4 L

22.4 L of  $N_2$  = volume occupied by 1 mole of  $N_2$  = 28 g =  $6.023 \times 10^{23}$  molecules

similarly

$O_2 = 2 \times 16 = 32 \text{ g}$ ,  $32 \text{ g} = 6.023 \times 10^{23}$  molecules = 22.4 L

$$22.4 \text{ L} = 6.023 \times 10^{23}$$

$$5.6 \text{ L} = \frac{6.023 \times 10^{23} \times 5.6}{22.4} \times 1 \times 6.023 \times 10^{23}$$

According to Avogadro's hypothesis, equal volume of all gases contain equal number of molecules under similar conditions of temperature and pressure.

133. Both A and R are false.

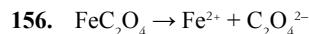
Number of g molecules or mole molecules

= wt. of Sub./GMM

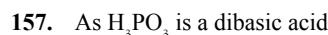
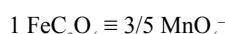
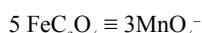
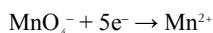
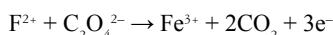
$$\text{SO}_2\text{Cl}_2 = 135 \text{ g (GMM)}$$

$$\text{So number of gm molecules} = \frac{13.5}{135} = 0.1$$

### The IIT-JEE Corner



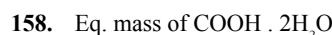
$\text{MnO}_4^-$  oxidizes  $\text{Fe}^{2+}$  and  $\text{C}_2\text{O}_4^{2-}$  both



So its molecular weight = 2 × equivalent wt.

$$1 \text{ M} = 2\text{N}$$

$$0.3 \text{ M} = 2 \times 0.3 = 0.6 \text{ N}$$



$$= \frac{\text{Mol mass}}{\text{basicity}} = \frac{126}{2} = 63$$

so normality of oxalic acid solution

$$= \frac{6.3 \times 1000}{63 \times 250} = 0.4 \text{ N}$$

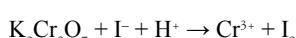
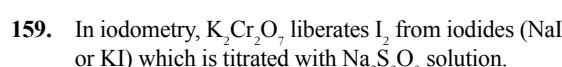
$$\text{N}_1\text{V}_1 = \text{N}_2\text{V}_2$$

$$\text{NaOH} \quad \text{oxalic acid}$$

$$1.1 \times \text{V1} = 0.4 \times 10 \text{ mL}$$

on solving

$$\text{V}_1 = 40 \text{ mL}$$



Here, one mole of  $\text{K}_2\text{Cr}_2\text{O}_7$  accepts 6 mole of electrons.

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{6}$$

160. As Mass of one electron =  $9.108 \times 10^{-31}$  kg So 1 kg of electrons =  $1/9.108 \times 10^{-31}$

$$= \frac{10^{31}}{9.108 \times 6.022 \times 10^{23}} \text{ mol}$$

$$= \frac{10^{31-23}}{9.108 \times 6.022} \text{ mole}$$

$$= \frac{10^8}{9.108 \times 6.022} \text{ mol}$$

161. Here

24 g of C-12 contain =  $2 \times 6.022 \times 10^{23}$  atoms

56 of Fe-56 contain =  $6.022 \times 10^{23}$  atoms

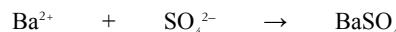
27 g of Al-27 contain =  $6.022 \times 10^{23}$  atoms

108 g of Ag-108 contain =  $6.022 \times 10^{23}$  atoms here

24 g of C-12 contains maximum number of atoms as it has maximum moles (2).



Excess 0.01 mole 0.01 mole



Excess 0.01 mole 0.01 mole



n factor of  $\text{Cr}_2\text{O}_7^{2-}$  = 6

n factor of  $\text{Fe}^{2+}$  = 1

So to reduce one mole of dichromate 6 moles of  $\text{Fe}^{2+}$  are required.

164.  $\bar{A} = \frac{\sum A_i x_i}{\sum x_i}$

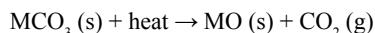
$$\bar{A} = 54 \times 0.05 + 56 \times 0.90 + 57 \times 0.5 \text{ (where } \bar{A} \text{ is atomic mass of Fe)}$$

$$\bar{A} = 55.95$$

## Numericals for Practice

1. In photosynthesis  $\text{CO}_2$  (g) and  $\text{H}_2\text{O}$  (l) are converted into glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$  (a sugar), and  $\text{O}_2$ . If 0.256 mol of  $\text{C}_6\text{H}_{12}\text{O}_6$  is formed by the reaction of  $\text{CO}_2$  with water, how many grams of  $\text{CO}_2$  would be needed?
- 0.256 g
  - 67.6 g
  - 33.8 g
  - 76.6 g
2. What is the percentage yield of  $\text{C}_2\text{H}_2$  when 50.0 g of  $\text{CaC}_2$  (s) (molar mass = 64.01 g) reacts with an excess of water to yield 13.5 g of  $\text{C}_2\text{H}_2$  (molar mass = 26.04 g) according to the following reaction:
- $$\text{CaC}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{s}) + \text{C}_2\text{H}_2(\text{g})$$
- 33.3 %
  - 86.5 %
  - 66.5 %
  - 56.6 %
3. How many moles of  $\text{KClO}_3$  are required to produce 2.51 g of  $\text{O}_2$ ? (Mass of one mole: K = 39.1 g, Cl = 35.5 g, O = 16.0 g)
- $$2\text{KClO}_3 \rightarrow 2\text{KCl} + 3\text{O}_2$$
- $5.23 \times 10^{-2}$  mol
  - $2.53 \times 10^{-1}$  mol
  - $1.53 \times 10^{-2}$  mol
  - $1.84 \times 10^{-1}$  mol
4. What is the per cent yield if 25.0 g of  $\text{I}_2$  is formed when 130.0 g of  $\text{HNO}_3$  reacts with 285.0 g of HI as follows:
- $$2\text{HNO}_3 + 6\text{HI} \rightarrow 2\text{NO} + 3\text{I}_2 + 4\text{H}_2\text{O}$$
- 16.68 %
  - 4.42 %
  - 4.42 %
  - 8.84 %
5. A 3.000 g sample of a soluble chloride is titrated with 52.60 mL of 0.2000 M  $\text{AgNO}_3$ . What is the percentage of chloride in the sample?
- 24.86 %
  - 12.43 %
  - 32.43 %
  - 6.23 %
6. The allowable concentration level of vinyl chloride,  $\text{C}_2\text{H}_3\text{Cl}$ , in the atmosphere in a chemical plant is  $2.0 \times 10^{-6}$  g/L. How many molecules are present per litre?
- $1.47 \times 10^{16}$  m/L
  - $1.97 \times 10^{16}$  m/L
  - $2.97 \times 10^{16}$  m/L
  - $1.07 \times 10^{16}$  m/L
7. An oxybromate compound,  $\text{KBrO}_x$ , where x is unknown, is analysed and found to contain 52.92 % Br. What is the value of x?
- 1
  - 2
  - 3
  - 3.5
8. Consider a sample of calcium carbonate in the form of a cube measuring 1.25 in. on each edge. If the sample has a density of 2.71 g/cm<sup>3</sup>, how many oxygen atoms does it contain?
- $1.07 \times 10^{24}$
  - $3.14 \times 10^{24}$
  - $1.57 \times 10^{24}$
  - $0.785 \times 10^{23}$
9. How many kilograms of  $\text{CO}_2$  are obtained when a sample of 0.15 m<sup>3</sup> of  $\text{C}_8\text{H}_{18}$  (l), whose density is 0.69 g/mL, is combusted in air?
- $3.2 \times 10^2$  kg
  - $1.6 \times 10^2$  kg
  - $6.4 \times 10^2$  kg
  - $2.2 \times 10^2$  kg
10. A solution is made by mixing 50.0 mL of 6.00 M HCl, 100.0 mL of 1.00 M HCl, and enough water to make 250.0 mL of solution. What is the molarity of HCl in the final solution?
- 0.8 M
  - 3.2 M
  - 2.5 M
  - 1.6 M
11. Aluminium reacts with oxygen to give aluminium oxide
- $$4\text{Al}(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{Al}_2\text{O}_3(\text{s})$$
- If you have 6.0 mol of Al, how many moles of  $\text{O}_2$  are needed for complete reaction?
- 204 mole
  - 305 mole
  - 504 mole
  - 405 mole
12. 100 ml of  $\text{NaHC}_2\text{O}_4$  required 50 ml of 0.1 M  $\text{KMnO}_4$  solution in acidic medium. Volume of 0.1 M NaOH required by 100 ml of  $\text{NaHC}_2\text{O}_4$  is.
- 25 ml
  - 75 ml
  - 125 ml
  - 135 ml
13. Menthol, from oil of mint, has a characteristic cool taste. The compound contains only C, H and O. If 95.6 mg of menthol burns completely in  $\text{O}_2$ , and gives 269 mg of  $\text{CO}_2$  and 110 mg of  $\text{H}_2\text{O}$ , what is the empirical formula of menthol?
- - 
  - $\text{C}_{10}\text{H}_{20}\text{O}$
  -

14. In an experiment, 1.056 g of a metal carbonate containing an unknown metal M, is heated to give the metal oxide and 0.376 g CO<sub>2</sub>.



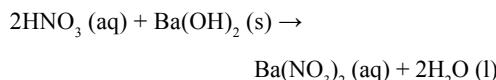
What is the identity of the metal M?

- |       |       |
|-------|-------|
| a. Zn | b. Ni |
| c. Ba | d. Cu |

15. Titanium (IV) oxide (TiO<sub>2</sub>) is heated in hydrogen gas to give water and a new titanium oxide, Ti<sub>x</sub>O<sub>y</sub>. If 1.598 g of TiO<sub>2</sub> produces 1.438 g of Ti<sub>x</sub>O<sub>y</sub>, what is the formula of the new oxide?

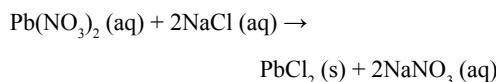
- |                     |                                   |
|---------------------|-----------------------------------|
| a. TiO <sub>3</sub> | b. Ti <sub>2</sub> O <sub>3</sub> |
| c. TiO <sub>2</sub> | d. Ti <sub>3</sub> O <sub>2</sub> |

16. What volume of 0.125 M HNO<sub>3</sub> in milliliters, is required to react completely with 1.30 g of Ba(OH)<sub>2</sub>?



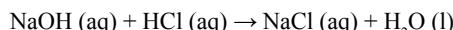
- |           |            |
|-----------|------------|
| a. 121 ml | b. 221 ml  |
| c. 242 ml | d. 60.5 ml |

17. What volume of 0.750 M Pb(NO<sub>3</sub>)<sub>2</sub>, in milliliters, is required to react completely with 1.00 L of 2.25 M NaCl solution? The balanced equation is



- |                         |                            |
|-------------------------|----------------------------|
| a. $1.0 \times 10^3$ ml | b. $3.0 \times 10^{-3}$ ml |
| c. $1.5 \times 10^3$ ml | d. $1.5 \times 10^{-3}$ ml |

18. What volume of 0.812 M HCl, in milliliters, is required to titrate 1.33 g of NaOH to the equivalence point?



- |            |            |
|------------|------------|
| a. 20.4 ml | b. 40.9 ml |
| c. 80.9 ml | d. 409 ml  |

19. When one gram mole of KMnO<sub>4</sub> reacts with HCl, the volume of chlorine liberated at NTP will be:

- |             |             |
|-------------|-------------|
| a. 16.5 lit | b. 22.4 lit |
| c. 52.0 lit | d. 56 lit   |

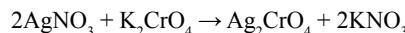
20. What is the molarity of KNO<sub>3</sub> in a solution prepared by dissolving 3.765 grams of KNO<sub>3</sub> in enough water to make 375 millilitres of solution?

- |           |           |
|-----------|-----------|
| a. 0.2482 | b. 0.1241 |
| c. 0.062  | d. 1.12   |

21. What is the molarity of a 20.00 % solution of sodium nitrate (NaNO<sub>3</sub>)? The solution density is 1.143 g/mL.

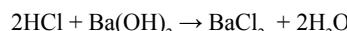
- |          |         |
|----------|---------|
| a. 2.40  | b. 4.68 |
| c. 0.468 | d. 2.68 |

22. How many grams of AgNO<sub>3</sub>, are required to react with 75.00 millilitres of 0.420 M K<sub>2</sub>CrO<sub>4</sub>?



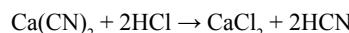
- |            |            |
|------------|------------|
| a. 5.355 g | b. 1.071 g |
| c. 10.71 g | d. 21.42 g |

23. What is the molarity of a barium hydroxide solution if 15.48 millilitres of it are required to react with 25.00 millilitres of 0.3026 M HCl solution?



- |             |             |
|-------------|-------------|
| a. 0.2443 M | b. 0.1225 M |
| c. 2.443 M  | d. 0.36 M   |

24. The poisonous gas hydrogen cyanide can be produced by treating cyanide compounds with acid. How many grams of HCN could be produced from the reaction of 28.0 grams of Ca(CN)<sub>2</sub> and 28.0 grams of HCl?



- |           |           |
|-----------|-----------|
| a. 8.2 g  | b. 32.6 g |
| c. 16.4 g | d. 64.8 g |

25. If 2.82 grams of CCl<sub>4</sub> are produced from the reaction of 2.25 grams of CS<sub>2</sub> with 14.60 grams of Cl<sub>2</sub>, what per cent yield of CCl<sub>4</sub> is obtained?

- |         |         |
|---------|---------|
| a. 31 % | b. 62 % |
| c. 46 % | d. 88 % |

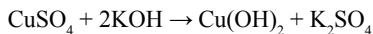
26. Which has highest molarity of the solute in the solution that results when the following mixtures are prepared?

- |                                                                                        |
|----------------------------------------------------------------------------------------|
| a. 200.0 ml of water is added to 30.0 ml of 6.00 M NaOH                                |
| b. 600.0 ml of water is added to 20.0 ml of 0.480 M NaOH solution                      |
| c. 300.0 ml of 12.0 M HNO <sub>3</sub> is added to 100.0 ml of 3.00 M HNO <sub>3</sub> |
| d. 30.0 ml of 0.800 M KBr is added to 80.0 ml of 0.350 M KBr                           |

27. What volume of 0.407 M KOH solution is just sufficient to react completely with 3.16 grams of CuSO<sub>4</sub>.5H<sub>2</sub>O according to the equation below?

## 1.62 ■ Mole Concept and Stoichiometry

The  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  dissolves as the KOH is added to form aqueous  $\text{CuSO}_4$ .



- a. 31.1 ml      b. 62.2 ml  
 c. 93.6 ml      d. 6.22 ml

28. What is the per cent by mass of  $\text{HNO}_3$  in an aqueous 7.911 M  $\text{HNO}_3$  solution if the solution has a specific gravity of 1.249?

- a. 40 %      b. 56 %  
 c. 32 %      d. 88 %

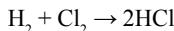
29. How many grams of  $\text{NaCl}$  are needed to make 675 grams of 2.55 % by mass  $\text{NaCl}$  solution?

- a. 8.6 g      b. 1.72 g  
 c. 17.2 g      d. 3.4 g

30. Calculate the volume of  $\text{CO}_2$  produced by the combustion of 40 ml of acetone vapours in presence of excess of oxygen.

- a. 120 ml      b. 1.20 ml  
 c. 12 ml      d. 20 ml

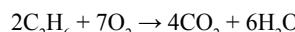
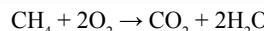
31. If 74.30 g of  $\text{HCl}$  were produced from 2.130 g of  $\text{H}_2$  and an excess of  $\text{Cl}_2$  according to the reaction



What was the per cent yield of  $\text{HCl}$ ?

- a. 48.22 %      b. 192.88  
 c. 96.44 %      d. 66.44 %

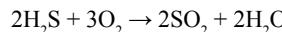
32. A mixture of composition 70.0 % methane and 30.0 % ethane ( $\text{C}_2\text{H}_6$ ) by mass is burned in oxygen to produce  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The reactions that occur are



How many grams of  $\text{O}_2$  are needed to react completely with 75.0 g of mixture?

- a. 294 g      b. 147 g  
 c. 588 g      d. 197 g

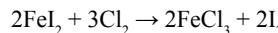
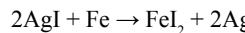
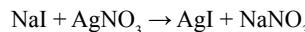
33. Hydrogen sulphide burns in oxygen to form sulphur dioxide and water



How many grams of hydrogen sulphide must react in order to produce a total of 100.0 of products?

- a. 14.53 g      b. 20.76 g  
 c. 83.06 g      d. 41.53 g

34. The following process has been used for obtaining iodine from oilfield brines



How much  $\text{AgNO}_3$ , in grams is required in the first step for every 5.00 g of  $\text{I}_2$  produced in the third step?

- a. 6.69 g      b. 3.34 g  
 c. 13.28 g      d. 16.69 g

35. 20 ml of 'X' M  $\text{HCl}$  neutralizes 5 ml of 0.2 M  $\text{Na}_2\text{CO}_3$  solution to phenolphthalein end point. The value of 'X' is.

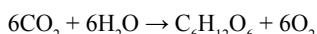
- a. 0.05 M      b. 0.126 M  
 c. 0.184 M      d. 0.150 M

### ANSWER KEYS

	Q.	Ans.								
	1.	b	2.	c	3.	a	4.	d	5.	b
	6.	b	7.	b	8.	c	9.	a	10.	d
	11.	d	12.	c	13.	c	14.	d	15.	b
	16.	a	17.	c	18.	b	19.	d	20.	b
	21.	d	22.	c	23.	a	24.	c	25.	b
	26.	c	27.	b	28.	a	29.	c	30.	a
	31.	c	32.	a	33.	d	34.	a	35.	a

## Hints and Explanations

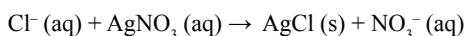
1. Chemical reaction is as follows:



$$\text{Grams CO}_2 = (0.256 \text{ mol C}_6\text{H}_{12}\text{O}_6)$$

$$\begin{aligned} & \times \frac{(6 \text{ mol CO}_2)}{(1 \text{ mol C}_6\text{H}_{12}\text{O}_6)} \times \frac{(44.01 \text{ g CO}_2)}{(1 \text{ mol CO}_2)} \\ & = 67.6 \text{ g CO}_2. \end{aligned}$$

5. The reaction is as follows:



$$\begin{aligned} \text{Grams Cl}^- &= (52.60 \text{ mL AgNO}_3) (1\text{L}/1000 \text{ ml}) \times \\ &(0.2000 \text{ mol AgNO}_3/1 \text{ L AgNO}_3) \times (1 \text{ mol Cl}^-/1 \\ &\text{mol AgNO}_3) \times (35.45 \text{ g Cl}^-/1 \text{ mol Cl}^-) \\ &= 0.3729 \text{ g Cl}^- \end{aligned}$$

% Cl<sup>-</sup> in sample

$$\begin{aligned} &= \frac{\text{Mass of Cl}^- \text{ in sample}}{\text{Sample mass}} \times 100 \\ &= 12.43 \% \end{aligned}$$

12.  $\text{NaHC}_2\text{O}_4 + \text{KMnO}_4 \rightarrow \text{Mn}^{2+} + \text{CO}_2$

Eq. of NaHC<sub>2</sub>O<sub>4</sub> = Eq. of KMnO<sub>4</sub>

$$0.1 \times M \times 2 = 0.05 \times 0.1 \times 5$$

$$M = \frac{0.25}{2} = 0.125$$

Mole of NaHC<sub>2</sub>O<sub>4</sub> = Mole of NaOH

$$\frac{0.25}{2} \times 0.1 = 0.1 \times V$$

$$V = 0.125 \text{ litre} = 125 \text{ ml.}$$

19.  $5 \times 1 = 2 \times n(\text{Cl}_2)$

$$n(\text{Cl}_2) = 5/2$$

$$V\text{Cl}_2 = \frac{5}{2} \times 22.4 \text{ lit} = 56 \text{ lit}$$

30.  $\text{CH}_3\text{COCH}_3 + 4\text{O}_2 \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O}$

$$V\text{CO}_2 = 3 \times 40 = 120 \text{ ml}$$

35.  $\text{Na}_2\text{CO}_3 + \text{HCl} \rightarrow \text{NaHCO}_3 + \text{NaCl}$

$$X \times 20 \times 10^3 = 0.2 \times 5 \times 10^{-3}$$

On solving, we get

$$X = 0.05$$

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## CHAPTER 2

# Gaseous and Liquid States

### Chapter Contents

Absolute scale of temperature, ideal gas equation; Deviation from ideality, van der Waal's equation; Kinetic theory of gases, average, root mean square and most probable velocities and their relation with temperature; Law of partial pressures; Vapour pressure; Diffusion of gases and Various levels of multiple-choice questions.

Matter is a substance having mass and volume. Matter has three states, solid, liquid and gas. Plasma is considered to be its fourth state.



Molecular interaction energy, thermal energy increases →

### CHARACTERISTICS OF GAS

Some of the important characteristics of a gas are as follows:

- (i) Composition of gases is always from non-metals. Example, O<sub>2</sub>, N<sub>2</sub>, He, Cl<sub>2</sub> etc.
- (ii) Gases always form a homogenous mixture regardless of the identities and proportions.
- (iii) Gases have high diffusibility, thermal expansion and high compressibility as there are

large empty spaces between molecules so on applying pressure molecules get closer.

(iv) Volume: Volume of the gas is equal to volume of the container in which gas is taken as a gas tries to occupy the entire available space. It is expressed in litres or m<sup>3</sup> or ml or cm<sup>3</sup> etc.

(v) Pressure: A gas can exert pressure on all the interior boundaries of the vessel due to molecular motion of its molecules which leads to collisions between these molecules and walls of the vessel. Gaseous pressure is measured by manometer while atmospheric pressure is measured by Barometer.

Gaseous pressure is measured in Newton per m<sup>2</sup> or nm Hg or atmosphere or torr.

$$1 \text{ atm} = 760 \text{ mm Hg or torr}$$

## 2.2 ■ Gaseous and Liquid States

$$= 1.013 \times 10^5 \text{ N/m}^2 \text{ or Pascal (Pa)}$$

$$= 1.013 \times 10^6 \text{ Dyne/cm}^2$$

$$= 1.013 \text{ bar}$$

- (vi) Mass: Mass of a gas can be determined by usual weight determination methods using weighing difference methods. It is related to number of moles of the gas.

$$n (\text{mole}) = \frac{W}{M}$$

Here W = Weight in gm.

M = Molar mass of the gas

- (vii) Temperature: Temperature of a gas tells the energetic level of the gaseous molecules.

Kinetic energy  $\propto$  Temperature.

The energy and velocity of gas molecules increase with the increase of temperature and their motion becomes random. At standard condition temperature is 298 K and pressure of gas is 1 atm and this is called Standard temperature and pressure state (STP or NTP).

- (viii) The molecules of gases have maximum energy and minimum force of attraction so they do not have a definite volume or shape.

- (ix) Gases have low densities and the density of gases with respect to hydrogen is called relative density.

**Vapour:** It is gaseous form of a solid or liquid at room temperature. Vapour state can be liquefied by increasing pressure while gaseous state can be liquefied by increasing pressure and decreasing temperature. A gas below its critical temperature is a vapour.

**Triple Point:** Solid, liquid and gas, all phases can exist together at a particular temperature and pressure, it is known as triple point. Example, at 4.58 mm pressure and 0.0098°C, water has all the three phases (Ice, vapour, water).

## GAS LAWS

As gases show their dependency on pressure, volume and temperature so the relationship of these factors can be explained through gas laws as follows:

**Boyle's Law:** According to it, "At constant temperature, the volume of a given mass of a gas is inversely proportional to its pressure." that is,

$$V \propto 1/P$$

$$\text{Or } V = K/P$$

Here K = constant

PV = constant (K) at constant temp.

$$\text{Or } \log_{10} P + \log_{10} V = \text{Constant (K)}$$

$$P_1 V_1 = P_2 V_2 \text{ (at constant temp.)}$$

Initial final

Conditions conditions

The differential form of Boyle's law can be written as

$$P \cdot \delta_V + V \cdot \delta_P = 0$$

So,

$$(dP/dV)_T = -P/V = -K/V^2$$

## Relation between Density and Pressure

According to Boyle's law at constant temperature and constant mass

$$V \propto 1/P \quad (\text{As T and mass are constant})$$

$$V \propto 1/d \quad (\text{Here d is the density})$$

As  $V = \text{Mass}/\text{density}$

$$\text{So } 1/d \propto 1/P$$

that is,  $d \propto P$  or  $d = K/P$

$$\text{or } \log_{10} P = \log_{10} 1/V + \log_{10} K$$

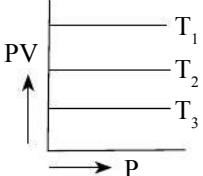
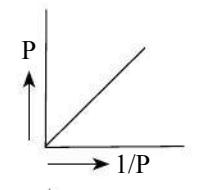
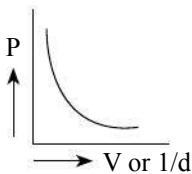
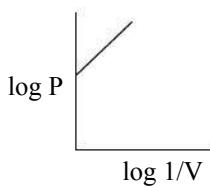
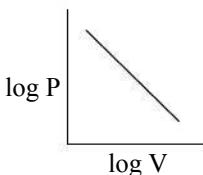
$$d_1/P_1 = d_2/P_2$$

### REMEMBER

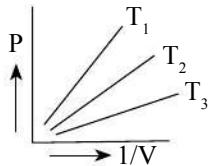
- Air at the sea level is dense as it is compressed by the mass of air present above it but the density and pressure decreases with the increase in altitude.
- The size of weather balloons becomes larger and larger as it rises or goes to higher altitude as the external pressures becomes lower and lower.

## Various Plots between Pressure vs Volume

These plots are called Isotherms.



Here  $T_1 > T_2 > T_3$



Here  $T_1 > T_2 > T_3$

## Illustrations

- A 1.103 L flask containing nitrogen at a pressure of 710.6 torr is connected to an evacuated flask of unknown volume. The nitrogen which acts ideally is allowed to expand into the combined system of both flasks isothermally.

If the final pressure of nitrogen is 583.1 torr, determine the volume of the evacuated flask.

**Solution** As the flasks are isothermally combined so temperature is constant. According to Boyle's law,

$$P_1 V_1 = P_2 V_2$$

$$(710.6 \text{ torr}) (1.103 \text{ L}) = (583.1 \text{ torr}) \times V_2$$

$$V_2 = \frac{710.6 \times 1.103}{583.1} \text{ L} = 1.344 \text{ L}$$

As  $V_2$  is final volume so the volume of evacuated flask is  $1.344 - 1.103 = 0.241 \text{ L}$ .

- Oxygen gas is commonly sold in 49.0 litre steel containers at a pressure of 150 atm. What volume (in litre) would the gas occupy at a pressure of 1.02 atm if its temperature remained unchanged? If its temperature was raised from  $20.0^\circ\text{C}$  to  $35.0^\circ\text{C}$  at constant  $P = 150 \text{ atm}$ ?

**Solution** As  $n$  and  $T$  are constant,

$$\text{Therefore } nRT = P_i V_i = P_f V_f$$

$$V_f = \frac{P_i V_i}{P_f} = \frac{150 \times 49.0}{1.02}$$

$$= 7210 \text{ litre}$$

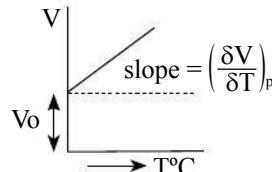
As  $n$  and  $P$  are constant

$$\text{Therefore } \frac{nR}{P} = \frac{V_i}{T_i} = \frac{V_f}{T_f}$$

$$V_f = \frac{V_i T_f}{T_i} = \frac{49.0 \times 308}{293} = 51.5 \text{ litre}$$

## Charle's Law

In order to explain it, let us consider the following plot between volume and temperature.



It shows that the volume of a definite amount of a gas varies linearly with temperature on Celsius scale.

It can be given as  $V_t = a + bt$

Here  $a$  and  $b$  are constant

## 2.4 ■ Gaseous and Liquid States

$$a = V_0 \text{ at } 0^\circ\text{C}$$

$$b = \text{slope} (\partial V / \partial T)_p$$

So according to Charle's law, "At constant pressure, the volume of a given mass of a gas increases or decreases by 1/273 of its volume of  $0^\circ\text{C}$  for every one degree centigrade rise or fall in temperature" that is,

$$V_t = V_0 + \frac{V_0}{273} \times t^\circ\text{C} \text{ (at const. temp.)}$$

$$= V_0 (1 + t^\circ\text{C}/273) = V_0 (273 + t^\circ\text{C}/273)$$

$$= V_0 \frac{T}{273}$$

Therefore

$V \propto T$  or  $V \propto T$  at constant pressure i.e.,

$$\text{Or } \boxed{V/T = \text{constant}}$$

Hence "At constant pressure, the volume of a given mass of a gas is directly proportional to its temperature in Kelvin."

$$\boxed{\frac{V_1}{T_1} = \frac{V_2}{T_2}} \quad \text{At constant pressure}$$

### Relation between Density and Temperature

As  $V \propto 1/d$  ( $d$  = density), So

$$V \propto T$$

$$\text{So } d \propto T = \text{constant}$$

$$\text{that is, } \boxed{d_1 T_1 = d_2 T_2}$$

### REMEMBER

Charle's Law is not applicable to liquids.

### Volume Coefficient ( $\alpha_v$ )

It represents the ratio of increase in volume of a gas at constant pressure per degree rise of temperature to its volume at  $0^\circ\text{C}$ . Its value is  $1/273$  for all gases.

$$\alpha_v = \frac{V_t - V_0}{V_0 \times t^\circ\text{C}}$$

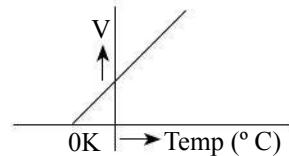
### Absolute Scale of Temperature or Absolute Zero

As according to Charle's law  $V_0 (1 + t^\circ\text{C}/273)$

If the temperature of a gas is lowered upto  $-273^\circ\text{C}$  the volume of the gas becomes zero. This temperature is known as absolute zero and this zero point on the scale is called as Kelvin scale.

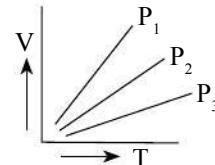
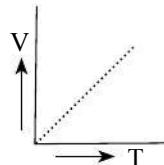
The absolute value of this temperature is  $-273.15^\circ\text{C}$ . At this temperature, pressure, kinetic energy and heat content of the gas is also zero. Absolute zero does not indicate thus volume of the gas is zero. There is no significance of gas laws at this temperature as gas phase is not observed here as a gas liquefied or solidified before this temperature.

When a graph is plotted between the volume of the gas against this temperature at constant pressure, it is called isobar and it is always a straight line.



### Plots between V vs T

These are called Isobars.



$$\text{Here } P_1 < P_2 < P_3$$

$$\text{As } P \propto T$$

### Illustrations

3. A flask is of a capacity of one litre. What volume of air will escape from the flask if it is heated from  $27^\circ\text{C}$  and  $37^\circ\text{C}$ ? Assume pressure to be constant.

**Solution**  $T = 27^\circ\text{C} = 300\text{ K}$

$$T_1 = 37^\circ\text{C} = 310\text{ K}$$

$$V = 1 \text{ litre,}$$

$$V_1 = ?$$

$$\frac{V}{T} = \frac{V_1}{T_1} \text{ (At constant pressure)}$$

$$\frac{1}{300} = \frac{V_1}{310}$$

$$V_1 = \frac{310}{300} = 1.0333 \text{ litre}$$

As capacity of flask is 1 litre.

So volume of air escaped out =  $1.033 - 1$   
 $= 33.3 \text{ ml.}$

4. To what temperature must an ideal gas be heated under isobaric conditions to increase the volume from  $100 \text{ cm}^3$  at  $25^\circ\text{C}$  to  $1.00 \text{ dm}^3$ ?

**Solution** According to the Charle's law,

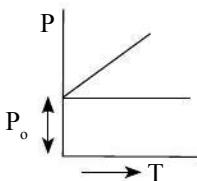
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{100 \text{ cm}^3}{300 \text{ K}} = \frac{1.00 \times 10^3 \text{ cm}^3}{T_2}$$

$$T_2 = \frac{1000 \times 298}{100} = 2980 \text{ K}$$

$$\text{Temperature} = 2980 - 273 = 2707^\circ\text{C}$$

**Pressure-Temperature Law (Gay-Lussac's Law)** In order to explain it, let us consider



It shows that the pressure of a definite amount of a gas at constant volume varies linearly with temperature on Celsius scale.

It can be given as  $P_t = a + bt$

Here  $a$  and  $b$  are constant

$$a = P_0 \text{ at } 0^\circ\text{C}$$

$$b = \text{slope } (\partial P / \partial T)_V$$

According to pressure- temperature law "At constant volume, the pressure of a given mass of a gas increases or decreases by  $1/273$  of its pressure at  $0^\circ\text{C}$  for every  $1^\circ\text{C}$  rise or fall in temperature," that is,

$$P_t = P_0 + \frac{P_0}{273} \times t^\circ\text{C}$$

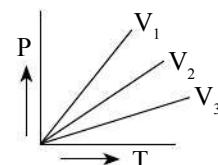
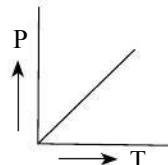
$$= P_0 \frac{(273 + t^\circ\text{C})}{273} = P_0 \frac{T}{273}$$

$$P \propto T \text{ that is, } \frac{P}{T} = \text{constant}$$

At constant volume

$$\boxed{\frac{P_1}{T_1} = \frac{P_2}{T_2}}$$

### Plots between P vs T



Here  $V_3 > V_2 > V_1$   
 $\text{As } V \propto T \text{ (i.e. } T_1 < T_2 < T_3\text{)}$

Here curves are called Isochors and the slope will be greater for lower volumes.

### Pressure Coefficient ( $\alpha_p$ )

It represents the ratio of increase in pressure of the gas at constant volume per degree rise of temperature to its pressure at  $0^\circ\text{C}$ . Its value is  $1/273$  for all gases.

$$\alpha_p = \frac{P_t - P_0}{P_0 \times t^\circ\text{C}}$$

### Avogadro's Law

According to Avogadro's law, "At constant temperature and pressure, equal volume of gases will have same number of molecules or moles."

$$V \propto N \text{ or } n$$

$$V/n = \text{constant}$$

$$\boxed{\frac{V_1}{N_1} = \frac{V_2}{N_2}}$$

$$\boxed{\frac{V_1}{N_1} = \frac{V_2}{N_2}}$$

Here  $n = \text{Number of moles of gas used}$

$N = \text{Number of molecules of gas used}$

### Molar Volume or Gram Molecular Volume

1 mole of a gaseous substance has 22.4 litre volume at NTP which is known as it's molar volume.

## 2.6 ■ Gaseous and Liquid States

### Avogadro Number

1 mole of a substance contains  $6.02 \times 10^{23}$  number of molecules.

- 1 gram atom of any element contains  $6.02 \times 10^{23}$  atoms.

$$\text{Hence } N_A = 6.02 \times 10^{23}$$

### REMEMBER

Avogadro law is applicable under the conditions of high temperature and low pressure that is, for an ideal gas.

### Combined Gas Laws and Ideal Gas Equation

On combining Boyle's, Charle's and other gas laws we get

$$\text{As } V \propto \frac{1}{P} \quad [\text{Boyle's law}]$$

$$V \propto T \quad [\text{Charle's law}]$$

$$V \propto n \quad [\text{Avogadro law}]$$

$$\text{So } V \propto \frac{nT}{P}$$

$$\text{Or } PV \propto nT$$

$$\text{Or } PV = nRT = nST$$

$$PV = \frac{w}{M} RT$$

$$P = \frac{w}{MV} RT$$

$$P = CRT \quad [\text{As } C = \frac{w}{MV}]$$

$$P = \frac{d}{M} RT \quad [\text{As } d = w/V]$$

- R or S : Molar gas constant or universal gas constant

Values of R = 0.0821 lit, atm, K<sup>-1</sup>, mol<sup>-1</sup>

$$= 8.314 \text{ joule K}^{-1} \text{ mol}^{-1}$$

$$= 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

$$= 2 \text{ cal K}^{-1} \text{ mol}^{-1}$$

- For a single molecule, gas constant is known as Boltzmann constant (k).

$$k = R/N_A$$

$$= 1.38 \times 10^{-23} \text{ J/deg-abs/molecule}$$

$$= 1.38 \times 10^{-16} \text{ erg/deg-abs/molecule}$$

$$\text{As } \frac{PV}{T} = \text{constant}$$

So Ideal gas equation can be written as

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

### Illustrations

- How large a balloon could you fill with 4.0 g of He gas at 22°C and 720 mm of Hg?

**Solution** P = 720/760 atm

$$T = 295 \text{ K}$$

$$w = 4 \text{ g}$$

$$m = 4 \text{ (He)}$$

$$PV = \frac{w}{m} RT$$

$$V = \frac{w RT}{m \times P} = \frac{4 \times 0.0821 \times 295 \times 760}{4 \times 720}$$

$$= 25.565 \text{ litre}$$

- Calculate the density of CO<sub>2</sub> at 100°C and 800 mm Hg pressure.

**Solution** P = 800/760 atm

$$T = 373 \text{ K}$$

$$PV = \frac{w}{m} RT$$

$$P = \frac{d}{m} RT \quad (\text{As } w/v = \text{density})$$

$$\frac{800}{760} = \frac{d}{44} \times 0.0821 \times 300$$

$$d = 1.5124 \text{ g litre}^{-1}$$

- When 2 g of a gusions substance P is introduced into an initially evacuated flask kept at 25°C the pressure is found to be 202.65 kPa. The flask is evacuated and 3 g of Q<sub>(g)</sub> is introduced as a result the pressure become 101.325 kPa at 298 k. How much time Q is heavier than P here?

**Solution** As PV =  $\frac{W}{M} RT$

$$\text{For Gas 'P' } \rightarrow 202.65 \times V = \frac{2 \times 10^{-3}}{M_p} \times R \times T \quad \dots \dots \dots \quad 1$$



## 2.8 ■ Gaseous and Liquid States

The molecular masses of gases A and B are  $M_A$  and  $M_B$  respectively.

$$M_A = \frac{2RT}{(1 \text{ atm})V}.$$

$$M_B = \frac{3RT}{(0.5 \text{ atm})V}.$$

$$\frac{M_A}{M_B} = \frac{2RT}{1 \text{ atm} \times V} \times \frac{0.5 \text{ atm} \times V}{3RT} = \frac{1}{3}$$

$$M_A : M_B = 1 : 3.$$

### Dalton's Law of Partial Pressure

According to Dalton's law, "Total pressure of a mixture of non-reacting gases is equal to the sum of partial pressure of these gases at constant temperature and constant volume."

$$P_{\text{mix}} = P_1 + P_2 + P_3 \dots$$

Here  $P_{\text{mix}}$  = pressure of the gaseous mixture

$P_1, P_2, P_3$  = partial pressure of gases

$$\text{Partial pressure of any gas} = \frac{\% \text{ of that gas}}{100} \times P_{\text{mix}}$$

% of a gas in a mixture

$$= \frac{\text{Partial pressure of the gas}}{\text{Total pressure of gaseous mixture}} \times 100$$

■ Partial pressure of any component A is given as

$$P_A = \frac{\text{moles of A}}{\text{Total moles}} \times P_{\text{Total}}$$

■ Total pressure of a mixture having different components is given as

$$P_{\text{mix}} = (n_1 + n_2 + n_3 \dots) \frac{RT}{V}$$

$$P_{\text{mix}} = \left( \frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3} \right) \dots \frac{RT}{V}$$

Here  $w_1, w_2, w_3$  = weight of components or non-reacting gases and  $m_1, m_2, m_3$  are their molar masses.

T = Temperature in Kelvin.

V = Volume in litre.

■ When a gas is collected over water it mixes with water vapours so the correct pressure of moist gas is given as

$$P(\text{moist gas}) = P(\text{dry gas}) + P(\text{V.P. of water})$$

$$P(\text{dry gas}) = P(\text{moist gas}) - P(\text{V.P. of water})$$

Aqueous tension = Partial pressure of water vapour in moist gas.

■ Vapour pressure of water varies with temperature. Example, At  $0^\circ\text{C}$  it is 4.6 torr while at  $25^\circ\text{C}$  it is 23.8 torr.

### REMEMBER

Dalton's law is not applicable for a mixture of reacting gases like  $\text{N}_2$  and  $\text{O}_2$ ,  $\text{SO}_2$  and  $\text{O}_2$ .

### Illustrations

12. Calculate the total pressure in a 10 litre cylinder which contains 0.4 g of helium, 1.6 g of oxygen and 1.4 g of nitrogen at  $27^\circ\text{C}$ . Also calculate the partial pressure of helium gas in the cylinder. Assume ideal behaviour of gases. Given  $R = 0.082 \text{ litre atm K}^{-1} \text{ mol}^{-1}$ .

**Solution** Given  $V = 10 \text{ litre}$

$$\text{Mole of He} = 0.4/4 = 0.1$$

$$\text{Mole of O}_2 = 1.6/32 = 0.05$$

$$\text{Mole of N}_2 = 1.4/28 = 0.05$$

$$\text{Total mole} = 0.1 + 0.05 + 0.05 = 0.2$$

$$\text{As } PV = nRT$$

$$P_{\text{total}} = \frac{n RT}{V} = \frac{0.2 \times 0.082 \times 300}{10}$$

$$= 0.492 \text{ atm}$$

$$P_{\text{He}} = \text{Mole fraction of He} \times \text{Total pressure}$$

$$= \frac{0.1}{0.2} \times 0.492 = 0.246 \text{ atm}$$

13. A special gas mixture used in bacterial growth chambers contains 1.00 % by weight  $\text{CO}_2$  and 99.0 %  $\text{O}_2$ . What is the partial pressure (in atmospheres) of each gas at a total pressure of 0.977 atm?

**Solution** Let the sample be 100 g.

$$\text{CO}_2 = 1.00 \text{ g}$$

$$O_2 = 99.0 \text{ g}$$

$$\text{mol CO}_2 = 1.00 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2}.$$

$$= 0.0227 \text{ mol CO}_2$$

$$\text{mol O}_2 = 99.0 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2}.$$

$$= 3.094 \text{ mol O}_2$$

$$n_{\text{total}} = 3.094 + 0.0227 = 3.117 \text{ mol}$$

$$X_{O_2} = \frac{3.094 \text{ mol}}{3.117 \text{ mol}} = 0.993$$

$$X_{CO_2} = \frac{0.0227 \text{ mol}}{3.117 \text{ mol}} = 0.00728$$

$$P_{O_2} = X_{O_2} \cdot P_{\text{total}}$$

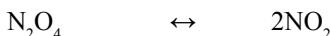
$$= 0.993 \times 0.977 = 0.970 \text{ atm}$$

$$P_{CO_2} = X_{CO_2} \cdot P_{\text{total}}$$

$$= 0.00728 \times 0.977 = 0.00711 \text{ atm}$$

14. 20% of  $N_2O_4$  molecules are dissociated in a sample of gas at  $27^\circ C$  and 760 torr. Calculate the density of the equilibrium mixture.

### Solution



$$1 \text{ mol} \quad 0 \quad \text{At } t = 0$$

$$(1 - 0.2) \text{ mol} \quad 0.4 \quad \text{At equilibrium}$$

$$\text{Total moles} = 0.8 + 0.4 = 1.2$$

$$PV = nRT$$

$$1 \times V = 1.2 \times 0.0821 \times 300$$

$$V = 29.556 \text{ litre}$$

$$d N_2O_4 = \frac{m}{V} = \frac{0.8 \times 92}{V \cdot 29.556} = 2.490$$

$$dNO_2 = m = 0.4 \times 46 = 0.6225 \text{ g/litre}$$

$$d_{\text{mix}} = 2.490 + 0.6225 = 3.113 \text{ g/litre.}$$

### Graham's Law of Diffusion

According to it "At constant pressure and temperature, the rate of diffusion of a gas is inversely proportional to the square root of its density or molecular weight" It is applicable only at low pressure.

$$r \propto \frac{1}{\sqrt{M}} \text{ or } \frac{1}{\sqrt{d}}$$

Here  $r$  = rate of diffusion or effusion of a gas or liquid.

$M$  and  $d$  are molecular weight and density respectively.

- For any two gases the ratio of rate of diffusion at constant pressure and temperature can be shown as  $r_1/r_2 = \sqrt{M_2/M_1}$  or  $\sqrt{d_2/d_1}$

If pressure are different and we take two gases then  $r_1/r_2 = P_1/P_2 \cdot (\sqrt{M_2/M_1} \text{ or } \sqrt{d_2/d_1})$

Hence diffusion or effusion of a gas or gaseous mixture is directly proportional to the pressure difference of the two sides and is inversely proportional to the square root of the gas or mixture effusing or diffusing out.

### Some other relations based on Graham's law

$$\text{As } r = V/t$$

= volume/time

So

$$\boxed{\frac{V_1 t_2}{V_2 t_1} = \sqrt{M_2/M_1}}$$

$$\text{As } r = \frac{n}{t} = \frac{d}{t} = \frac{w}{t}.$$

So

$$\boxed{\frac{n_1 t_2}{n_2 t_1} = \sqrt{M_2/M_1}}$$

$$\boxed{\frac{w_1 t_2}{w_2 t_1} = \sqrt{M_2/M_1}}$$

$$\boxed{\frac{d_1 t_2}{d_2 t_1} = \sqrt{M_2/M_1}}$$

Here  $n$  represents number of moles,  $w$  represents weight in gram and  $d$  represents distance travelled by a particular gas or liquid.

### Differentiation between Diffusion and Effusion

#### Diffusion

It is the movement of gaseous or liquid molecules without any porous bars that is, spreading of molecules in all directions.

## 2.10 ■ Gaseous and Liquid States

### Effusion

It is movement of gases molecules or liquid molecules through porous bar that is, a small hole or orifice.

### Uses of Graham's law

- Detecting the presence of Marsh gas in mines.
- Separation of isotopes by different diffusion rates. Example, U-235 and U-238
- Detection of molecular weight and vapour density of gases using this relation.

$$\frac{r_1}{r_2} = \left( \frac{m_2}{m_1} \right)^{1/2} \text{ or } \left( \frac{d_2}{d_1} \right)^{1/2}$$

### Illustrations

15. What is the molecular mass of a gas that diffuses through a porous membrane 1.86 times faster than Xe? What might the gas be?

**Solution**  $r_{Xe}/r_Z = \sqrt{(M_Z/M_{Xe})}$

$$1/1.86 = \sqrt{(M_Z/131.29)}$$

$$\sqrt{M_Z} = \frac{\sqrt{131.29}}{1.86}$$

$$M_Z = \frac{131.29}{(1.86)^2} = 37.9 \text{ g/mol}$$

Molecular mass = 37.9 amu

So the gas may be F<sub>2</sub>.

16. 20 dm<sup>3</sup> of SO<sub>2</sub> diffuse through a porous partition in 60 sec. What volume of O<sub>2</sub> will diffuse under similar conditions in 30 seconds?

**Solution**  $r_{SO_2} = \frac{V_{SO_2}}{t_{SO_2}} = \frac{20}{60} = 0.333 \text{ dm}^3/\text{sec}$

$$r_{O_2} = \frac{V_{O_2}}{t_{O_2}} = \frac{V}{30} \text{ dm}^3/\text{sec}$$

$$r_{SO_2}/r_{O_2} = \sqrt{(M_{O_2}/M_{SO_2})}$$

$$0.333/V/30 = \sqrt{(32/64)}$$

$$V = 14.14 \text{ dm}^3$$

17. The rate of effusion of an unknown gas (X) through a pin hole is found to be 0.279 times the rate of effusion of hydrogen (H<sub>2</sub>) gas through the

same pin hole. If both gases are at STP. What is the molecular mass of the unknown gas?

**Solution**  $r_1/r_2 = \sqrt{(m_2/m_1)}$

Assume 1 and 2 stands for hydrogen gas and unknown gas respectively.

$$1/0.279 = \sqrt{(m_2/2)}$$

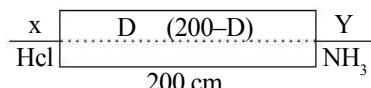
$$m_2 = \frac{2}{0.279 \times 0.279} = 25.7 \text{ g mol}^{-1}$$

18. A straight glass tube has two inlets X and Y at the two ends. The length of the tube is 200 cm. HCl gas through inlet X and NH<sub>3</sub> gas through inlet Y are allowed to enter the tube at the same time. White fumes first appear at a point P inside the tube. Find the distance of P from X.

**Solution** Molecular mass of HCl = 36.5

Molecular mass of NH<sub>3</sub> = 17.0

$$r_1/r_2 = \sqrt{(M_2/M_1)}$$



Assume the distance between P and X be D cm.

$$\frac{D}{(200 - D)} = \sqrt{(17/36.5)} = 0.6824$$

$$D = 0.6824 \times (200 - D)$$

$$D + 0.6824 D = 0.6824 \times 200$$

$$D = \frac{0.6824 \times 200}{1.6824} = 81.12 \text{ cm}$$

19. If an unknown homonuclear diatomic gaseous molecule effuses at a rate of 0.355 times to that of oxygen under similar conditions of temperature and pressure. Find the identity of this gas.

**Solution**  $r_g/r_{O_2} = \sqrt{(M_{O_2}/M_X)}$

$$0.355 = \sqrt{(32/M_X)}$$

$$M_X = \frac{32}{(0.355)^2} = 254$$

The molecular weight suggest that this homonuclear diatomic gaseous molecules I<sub>2</sub>.

20. Ammonia and the hydrogen chloride gases are introduced simultaneously at the ends of a 90 cm tube. At what distance ammonium chloride is formed from the end at which HCl is introduced?

**Solution** According to Graham's law of diffusion

$$r_1/r_2 = \sqrt{(d_2/d_1)} = \sqrt{(M_2/M_1)}$$

$$r_{\text{HCl}}/r_{\text{NH}_3} = \sqrt{(M_{\text{NH}_3}/M_{\text{HCl}})}$$

$$= \sqrt{(17/36.5)} = 4.123/6.040$$

$$r_{\text{HCl}} = 4.123 \text{ if } r_{\text{NH}_3} = 6.040$$

If the total length of the tube is 10.163 cm, HCl will travel 4.123 cm. If the total length of the tube is 90 cm, HCl will travel

$$= \frac{4.123}{10.163} \times 90 = 36.51 \text{ cm.}$$

So  $\text{NH}_4\text{Cl}$  is formed at a distance of 36.51 cm from the end where HCl is introduced.

## Kinetic Theory of Gases

Kinetic theory of gases was put forward by Bernoulli and was developed by Clausius and Kelvin.

- It was explained by Maxwell and Boltzmann.
- It is also known by other names, such as dynamic particle model and microscopic model.

## Main Assumptions

- (i) Each gas is composed of a large number of tiny particles called molecules and these molecules are identical in mass, size and shape.
- (ii) The volume of gaseous molecules is negligible to the volume of the gas.
- (iii) Molecules show random motion in straight lines in all possible directions but at a constant speed.
- (iv) Molecules undergo collisions which are perfectly elastic that is, no change in energy.
- (v) The force of attraction between molecules is negligible thus gas molecules can move freely and independent of each other.
- (vi) The effect of gravity on molecular motion is negligible.

- (vii) Pressure of the gas is due to collisions of molecules with the walls of the container.
- (viii) At any particular instance molecules have different speeds so have different kinetic energies, however, the average kinetic energy of these molecules is directly proportional to absolute temperature

Kinetic energy  $\propto$  absolute temperature

## Kinetic Gas Equation

On the basis of above assumptions it can be given as

$$PV = (1/3) mn u_{\text{r.m.s}}^2$$

Here P = pressure of gas

V = volume of gas

n = number of molecules of gas

$u_{\text{r.m.s}}$  = root mean square velocity (R.M.S)

## Kinetic Energy Calculation

As for one mole PV = RT

$$PV = 1/3 Mn u_{\text{r.m.s}}^2$$

$$\text{so } \frac{1}{3} Mu_{\text{r.m.s}}^2 = RT$$

$$u_{\text{r.m.s}}^2 = \frac{3RT}{M}$$

$$u_{\text{r.m.s}} = \sqrt{(3PV/M)} = \sqrt{(3RT/M)} = \sqrt{(3P/d)}$$

$$u_{\text{r.m.s}}^2 \propto T$$

$$u_{\text{r.m.s}} \propto \sqrt{T}$$

As from kinetic gas equation

$$\frac{1}{3} \frac{Mu_{\text{r.m.s}}^2}{N} = \frac{RT}{N}$$

As R/N = k

Here k = Boltzman constant

$$\frac{1}{3} mu_{\text{r.m.s}}^2 = kT$$

$$\frac{1}{2} mu_{\text{r.m.s}}^2 = \frac{3}{2} kT$$

$$\text{K.E.} = \frac{3}{2} kT$$

or

$$\boxed{\text{K.E.} = \frac{3}{2} \frac{RT}{N}}$$

## 2.12 ■ Gaseous and Liquid States

Here  $k$  is known as Boltzmann constant and its value is  $1.38 \times 10^{-16}$  erg.

### Illustrations

21. Find out the kinetic energy of 10 mol of gas at  $200^{\circ}\text{C}$ .

**Solution**  $\text{K.E.} = \frac{3}{2} \text{ RT}$

$$R = 8314 \times 10^7 \text{ erg/K/mol}$$

$$T = 200 + 273 = 473 \text{ K}$$

$n = 10$  moles of gas

$$\begin{aligned} \text{K.E.} &= \frac{3}{2} \times 10 \times 8314 \times 10^7 \times 473 \\ &= 58987.83 \times 10^7 \text{ erg.} \end{aligned}$$

22. Calculate the average kinetic energy in joules of the molecules in 8.0 g of methane at  $27^{\circ}\text{C}$ .

**Solution** As kinetic energy of the molecule

$$\text{K.E.} = \frac{3}{2} \text{ RT}$$

$$\text{So average K.E.} = n \left( \frac{3}{2} \text{ RT} \right)$$

Here  $n$  = Number of moles of the gas

$$\text{Molecular mass of CH}_4 = 12 + 4 = 16$$

Number of moles of CH<sub>4</sub> in 8.0 g

$$= \frac{8.0 \text{ g}}{16 \text{ g mol}^{-1}} = 0.5 \text{ mole}$$

$$\text{K.E.} = (0.5 \text{ mol}) \left( \frac{3}{2} \right) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (300\text{K})$$

$$= 1870.65 \text{ J.}$$

23. Find the pressure exerted by  $10^{23}$  gas molecules, each of mass  $10^{-25}$  kg, in a container of volume  $0.001 \text{ m}^3$  and having root mean square velocity of  $1000 \text{ ms}^{-1}$ . Also calculate total kinetic energy and temperature of gas.

**Solution** As  $P = \frac{1}{3} \frac{m N u^2}{V}$

$$= \frac{1 \times 10^{-25} \times 10^{23} \times (10^3)^2}{3 \times 10^{-3}}$$

$$= 3.33 \times 10^6 \text{ N m}^{-2}$$

$$\text{K.E.} = (\frac{1}{2} m u^2) \times N$$

$$= \frac{1}{2} \times 10^{-25} \times (10^3)^2 \times 10^{23} = \frac{1}{2} \times 10^4$$

$$= 0.5 \times 10^4 \text{ J}$$

$$\text{K.E.} = \frac{3}{2} n RT$$

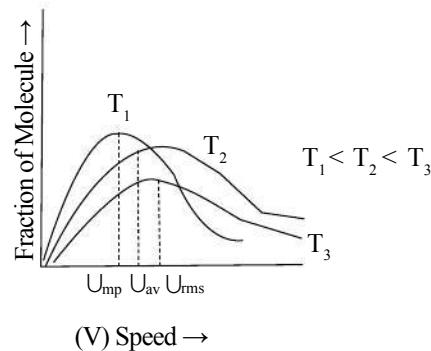
$$\text{Here } n \text{ (mole)} = \frac{10^{23}}{N_0}$$

$$= \frac{10^{23}}{6.023 \times 10^{23}}.$$

$$0.5 \times 10^4 = \frac{3}{2} \times \frac{10^{23}}{6.023 \times 10^{23}} \times 8.314 \times T$$

$$T = \frac{0.5 \times 10^4 \times 2 \times 6.023}{3 \times 8.314} = 2415 \text{ K}$$

### Molecular Speed Graph or Maxwell Distribution of Velocities



According to it

- Molecules have different speeds due to frequent molecular collisions with the walls and among themselves.
- Rare molecules have either very high or very low speed
- Maximum number of molecules of the gas have maximum velocity which is called most probable velocity and after Vmp velocity decreases
- Zero velocity is not possible.
- All these velocities increase with the increase in temperature but fraction of molecules having these velocities decreases.

### Different Velocity Terms

The Maxwell relation gives the fraction of molecules in one mole ( $d_N/N_A$ ) having a velocity in the Z-direction between  $U_z$  and  $U_z + dU_z$  as

$$\frac{d_N/N_A}{d U_z} = A e^{-m U^2 / 2 k T}$$

Here A = constant

$N_A$  = Avogadro number

The above relation in three dimensions can be written as

$$\frac{d_N/N_A}{d_U} = 4 \pi U^2 [M/2 \pi k T]^{3/2} e^{-m U^2 / 2 k T}$$

The velocity of gases can be expressed as follows:

(i) **Average Speed ( $\bar{u}$ )**: It is the average of different velocities possessed by the molecules.

$$U_{a.v.} = \frac{U_1 + U_2 + U_3}{n}$$

$$U_{a.v.} = \frac{n_1 U_1 + n_2 U_2 + n_3 U_3}{n_1 + n_2 + n_3}$$

Here  $n_1, n_2, n_3$  are the number of molecules having  $U_1, U_2, U_3$  velocities respectively.

■ Relation between  $U_{a.v.}$ , temperature and molar mass is given as

$$U_{a.v.} = \sqrt{(8RT/\pi M)} \\ = \sqrt{(8PV/\pi M)}$$

It is also denoted by  $\bar{u}$ .

(ii) **Root Mean Square Velocity ( $u_{r.m.s.}$ )**: It is square root of the mean of the square of the velocities of different molecules.

$$U_{r.m.s.} = \frac{\sqrt{(U_1^2 + U_2^2 + \dots)}}{n} \\ = \frac{\sqrt{(n_1 U_1^2 + n_2 U_2^2 + n_3 U_3^2)}}{n_1 + n_2 + n_3}$$

$$U_{r.m.s.} = \sqrt{(3RT/M)}$$

$$U_{r.m.s.} = \sqrt{(3PV/M)} \\ = \sqrt{(3P/d)}$$

(iii) **Most Probable Velocity ( $a$ )**: It is velocity possessed by maximum number of molecules.

$$U_{m.p.} = \sqrt{(2RT/M)} \\ = \sqrt{(2PV/M)}$$

■ These velocities increase with increase in temperature but the fraction of molecules having these velocities decreases.

### Relation between $\alpha$ , $\bar{u}$ and $u_{r.m.s.}$

$$\alpha : \bar{u} : u_{r.m.s.} =$$

$$\sqrt{(2RT/M)} : \sqrt{(8RT/\pi M)} : \sqrt{(3RT/M)}$$

$$= \sqrt{2} : \sqrt{(8/\pi)} : \sqrt{3}$$

$$= 1.414 : 1.595 : 1.732$$

$$= 1 : 1.128 : 1.224$$

$$= 0.8164 : 0.9213 : 1$$

that is,  $u_{r.m.s.} > \bar{u} > \alpha$ .

$$U_{a.v.} = U_{r.m.s.} \times 0.9213$$

$$\alpha (U_{m.p.}) = 0.8164 \times U_{r.m.s.}$$

### Illustrations

24. Find out the RMS velocity of  $O_2$  molecules at NTP (density of  $O_2 = 0.001429$  g/cc at NTP, density of Hg = 13.6 g /cc,  $g = 981$  cm/sec<sup>2</sup>).

**Solution**  $h = 76$  cm

$$u_{r.m.s.} = \sqrt{(3P/d)} = \sqrt{(3 \times h \times d \times g/d)} \\ = \frac{\sqrt{(3 \times 76 \times 13.6 \times 981)}}{\sqrt{0.001429}} \\ = 46137.6 \text{ cm sec}^{-1}$$

25. Two flasks A and B have equal volumes. Flask A contains  $H_2$  at 27°C while B contains equal mass of  $C_2H_6$  at 627°C. In which flask and by how many times are molecules moving faster? Assume ideal gas nature for both.

**Solution** For  $H_2$ , Average velocity

$$= \sqrt{(8RT/\pi M)} = \sqrt{(8R \times 300/\pi \times 2)}$$

For  $C_2H_6$  Average velocity

$$= \sqrt{(8RT/\pi M)} = \sqrt{(8R \times 900/\pi \times 30)}$$

$$\frac{\text{Average velocity } H_2}{\text{Average velocity } C_2H_6} = \frac{\sqrt{(300 \times 30)}}{\sqrt{(900 \times 2)}} \\ = 2.236 : 1$$

## 2.14 ■ Gaseous and Liquid States

26. Calculate the temperature at which the root mean square velocity of  $\text{SO}_2$  molecules is the same as that of  $\text{O}_2$  at  $27^\circ\text{C}$ .

**Solution**  $u = \sqrt{(3 RT_{\text{SO}_2}/M_{\text{SO}_2})} = \sqrt{(3 RT_{\text{O}_2}/M_{\text{O}_2})}$

$$\sqrt{(3 RT_{\text{SO}_2}/64)} = \sqrt{(3R \times 300/ 32)}$$

$$T_{\text{SO}_2} = 600 \text{ K}$$

27. Find the  $V_{\text{rms}}$  of a missed particle having a mass of  $10^{-12} \text{ g}$  at  $27^\circ\text{C}$  if value of Boltzmann constant  $k$  is  $1.31 \times 10^{-16} \text{ ergs per degree per molecule}$ .

**Solution**  $V_{\text{rms}} = \sqrt{(3kT/M)}$

$$= \frac{\sqrt{(3 \times 1.31 \times 10^{-16} \times 300)}}{\sqrt{10^{-12}}} \\ = 0.342 \text{ cm sec}^{-1}$$

28. Calculate the root mean square velocity of ozone kept in a closed vessel at  $20^\circ\text{C}$  and 82 cm mercury pressure.

**Solution** As given volumes are

$$V_1 = 22400 \text{ cm}^3, V_2 = ?$$

$$P_1 = 76 \text{ cm}, P_2 = 82 \text{ cm}$$

$$T_1 = 273 \text{ K}, T_2 = 273 + 20 = 293 \text{ K}$$

As

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

So

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$$

$$= \frac{76 \times 22400 \times 293}{273 \times 82} = 22282 \text{ cm}^3$$

Molecular mass of  $\text{O}_3 = 3 \times 16 = 48 \text{ g mol}^{-1}$

$$P = 82 \text{ cm} \times 13.6 \text{ g cm}^{-3} \times 981 \text{ cm sec}^{-2}$$

$$\text{So } u = \frac{\sqrt{(3PV)}}{\sqrt{M}}$$

$$= \frac{\sqrt{(3 \times 82 \times 13.6 \times 981 \times 22282)}}{\sqrt{(48)}}$$

$$= 3.90 \times 10^4 \text{ cm sec}^{-1}$$

### Ideal Gas

These gases obey gas laws under all the conditions of temperature and pressure.

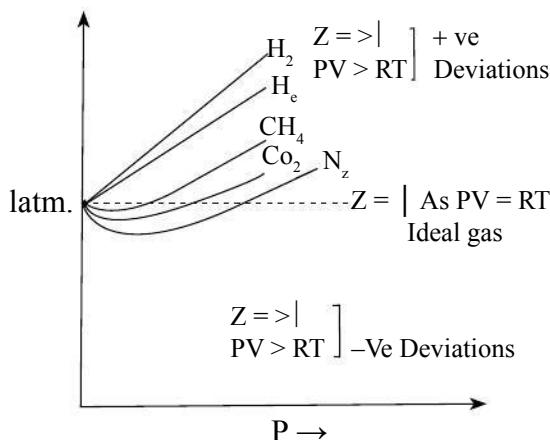
- No gas is ideal in reality (hypothetical).
- No force of attraction is present between molecules in them.
- Volume of molecules is negligible to the total volume of the gas (container).

### Real Gas

These gases obey gas laws only at high temperature and low pressure.

- All the gases are real.
- Here force of attraction between molecules cannot be neglected at high pressure and low temperature
- Here volume occupied by gas molecule is not negligible specially at high pressure and low temperature.

### Deviation of Real Gases from Ideal+ Gas Behaviour



- The extent of deviation of a real gas from ideal gas behaviour is expressed in terms of compressibility factor  $Z$ . It is an empirical correction for the non-ideal behaviour of real gases which allows the simple form of the combined gas law to be retained. It is given as

$$Z = \frac{PV}{nRT}$$

When  $Z = 1$  (ideal gas behaviour)

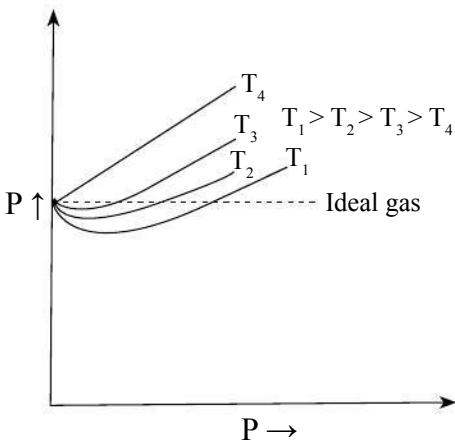
When  $Z < 1$  (negative deviations)

When  $Z > 1$  (positive deviations)

When  $Z < 1$  gas is more compressible

When  $Z > 1$  gas is less compressible

- For He and H<sub>2</sub>,  $Z > 1$  as  $PV > RT$  [as  $a/V^2 = 0$ ] that is, positive deviations.
- At Very Low Pressure :  $PV \approx RT$  (as  $a/V^2$  and  $b$  are neglected) that is,  $Z \approx 1$  so nearly ideal gas behaviour.
- At Low Pressure :  $PV < RT$  that is,  $Z < 1$  so negative deviation
- At Moderate Pressure :  $PV = RT$  i.e.,  $Z = 1$  so ideal gas behaviour.
- At High Pressure :  $PV > RT$  (as  $b$  can not be neglected). that is,  $Z > 1$  so positive deviation.
- An increase in temperature shows a decrease in deviation from ideal gas behaviour.



It shows that curve for a real gas has a tendency to coincide with that of an ideal gas at high temperatures. It means, at high temperatures, gases show ideal gas behaviour.

### Van der Waal's Equation

Van der waal's equation is a modification of the ideal gas equation that takes into account the non-ideal behaviour of real gases.

Van der Waal's equation modified kinetic theory of gases by considering these two points of kinetic theory of gases not to be fully correct or are not followed by real gases.

■ The force of attraction between gaseous molecules is negligible.

■ The volume of gaseous molecules is negligible to the total volume of the gas.

He made following two corrections:

**A. Volume Correction:** According to him, at high pressure the volume of the gas becomes lower so volume of molecules can not be ignored. Hence the actual space available inside the vessel for the movement of gas molecules is not the real volume of the gas, actually it is given as

$$V_{\text{real gas}} = V - b$$

Here  $V$  is the volume of the container while  $b$  is volume occupied by gas molecules and it is called co-volume or excluded volume.

The excluded volume for ' $n$ ' molecules of a gas =  $4nV_m$  or  $(4 \times 4/3 \pi r^3)$

Here  $V_m$  = Volume of one molecule ( $4/3 \pi r^3$ )

Now ideal gas equation can be written as -

$$P(V - b) = RT$$

$$P(V - nb) = nRT \dots\dots\dots (1)$$

**B. Pressure Correction:** According to him, at high pressure the gaseous molecules are closer so attraction forces cannot be ignored hence, pressure of the real gas is given as:

Pressure of the Real gas = pressure developed due to collisions ( $P$ ) + pressure loss due to attraction ( $p'$ )

$$P_{\text{real gas}} = P + p'$$

Here  $p'$  is pressure loss due to force of attraction between molecules or inward pull.

As :  $p' \propto n^2$  [ $n^2$  is number of molecules attracting or attracted]

$$p' \propto n^2 \propto d^2 \propto \frac{1}{V^2}$$

So

$$p' = \frac{a}{V^2} = \frac{a n^2}{V^2}$$

Here 'a' is van der waal's force of attraction constant,  $d$  is density and  $V$  is volume.

Hence

$$P_{\text{real gas}} = P + a/V^2$$

$$P + an^2/V^2 \dots\dots(2)$$

## 2.16 ■ Gaseous and Liquid States

Now ideal gas equation can be written after correction of pressure and volume as

For one mole

$$\left( P + \frac{a}{V^2} \right) \cdot (V - b) = RT$$

For n number of moles

$$\left( P + \frac{n^2 a}{V^2} \right) \cdot (V - nb) = nRT$$

### Units of a and b

$$a = \text{lit}^2 \text{ mol}^{-2} \text{ atm}$$

$$\text{or cm}^4, \text{ mol}^{-2} \text{ dyne}$$

$$\text{or m}^4 \text{ mol}^{-2} \text{ Newton}$$

$$b = \text{lit/mol}$$

$$\text{or cm}^3 / \text{mol}$$

$$\text{or m}^3 / \text{mol}$$

- The values of 'a' and 'b' are 0.1 to 0.01 and 0.01 to 0.001 respectively.

### Significance of a and b

- It gives the magnitude of attraction forces present between gas molecules.

Liquefaction of gases  $\propto a$

Hence more the value of 'a' or force of attraction between the molecules of a gas more will be its liquefaction: Example,

Values of 'a'



$$a \rightarrow (0.034) (0.244) (1.36) (1.39) (3.59) (3.8) (4.17) (6.71)$$

Increasing order of liquefaction of some gases

- Its constancy in value shows that gas molecules are incompressible.

$$b = 4N (4/3 \pi r^3)$$

- At low pressure 'a' dominates but at high pressure 'b' dominates.

### Limitations of Van der Waal's Equation

As the value of Van der Waal's constants 'a' and 'b' do not remain constant over the entire ranges of temperature and pressure so this equation is also valid over some specific ranges of temperature and pressure only.

### Van der waal's equation in terms of Compressibility Factor

$$\left[ P + \frac{n^2 a}{V^2} \right] [V - nb] = n RT$$

$$P = \frac{nRT}{(V - nb)} - \frac{a n^2}{V^2}$$

$$\text{As } Z = \frac{V_m}{V_m \text{ (ideal gas)}} = \frac{V_m}{n RT/P}$$

$$Z = \frac{PV_m}{nRT}$$

$$= \left[ \frac{nRT}{V_m - nb} - \frac{a n^2}{V_m^2} \right] \times \frac{V_m}{nRT}$$

$$Z = \frac{V_m}{V_m - nb} - \frac{an}{RTV_m}$$

### Explanations for Real Gas Behaviour

- At very low pressure for one mole of a gas, the value of 'p' and 'b' can be ignored so Van der Waal's equation becomes equal to ideal gas.

$$PV = RT$$

- At moderate pressure the value of 'nb' or 'b' can be ignored so Van der Waal's equation becomes

$$\left[ P + \frac{a}{V^2} \right] [V] = RT$$

$$PV + \frac{a}{V} = RT$$

$$PV = RT - \frac{a}{V}$$

$$\text{Hence } PV < RT$$

$$\text{So } Z = \frac{PV}{RT}$$

$$Z < 1$$

- At high pressure, the value of 'p' can be ignored so Van der Waal's equation can be written as

$$P(V - b) = RT$$

$$PV - Pb = RT$$

$$PV = RT + Pb$$

$$PV > RT$$

$$Z = \frac{PV}{RT}$$

$$\text{So } Z > 1$$

- In case of H<sub>2</sub>, He, p' is always ignored so for them Van der Waal's equation becomes

$$P(V - b) = RT$$

$$PV = RT + Pb$$

$$\text{i.e., } Z > 1$$

## Illustrations

29. 2 moles of ammonia occupied a volume of 5 litres at 27°C. Calculate the pressure if the gas obeyed Van der Waal's equation. ( $a = 4.17 \text{ atm lit}^2 \text{ mol}^{-2}$ ,  $b = 0.0371 \text{ lit mol}^{-1}$ )

**Solution**  $n = 2$ ,  $V = 5 \text{ litres}$ ,

$$T = 273 + 27 = 300 \text{ K}$$

$$R = 0.082 \text{ lit atm deg}^{-1} \text{ mole}^{-1}$$

$$\left( P + \frac{n^2 a}{V^2} \right) \cdot (V - nb) = nRT$$

$$[P + (4.17 \times 2^2/5^2)] [5 - 2 \times 0.037]$$

$$= 2 \times 0.082 \times 300$$

$$P = 9.33 \text{ atm}$$

30. Using Van der Waal's equation find the pressure (in atm) of 45 g of ammonia in a one liter vessel at 0°C, if for ammonia ' $a$ ' = 4.17 litre $^2$  atm mol $^{-2}$  and ' $b$ ' = 0.0371 litre mol $^{-1}$ .

**Solution** Moles of ammonia =  $\frac{45}{17} = 2.64$

Using Van der Waal's equation

$$\left( P + \frac{n^2 a}{V^2} \right) \cdot (V - nb) = nRT$$

$$\frac{P + (2.64)^2 \times 4.17}{1^2} \times (1 - 2.64 \times 0.0371)$$

$$= 2.64 \times 0.082 \times 273$$

On solving,

$$P = 36.5 \text{ atm}$$

31. If for nitric oxide (NO) the value of Van der Waal's constant  $b$  is 0.02788 litre mol $^{-1}$ . Find the diameter of NO.

**Solution**  $b = 4N \left( \frac{4}{3} \pi r^3 \right)$

$$\text{Here } b = 0.02788 \text{ litre/mol} = 27.88 \text{ cc/mole}$$

$$27.88 = 4 \times 6.023 \times 10^{23} \times \frac{4}{3} \times 3.14 \times r^3$$

$$r^3 = \frac{27.88 \times 3 \times 10^{-23}}{4 \times 6.023 \times 4 \times 3.14}$$

$$= 2.8 \times 10^{-8} \text{ cm}$$

32. Calculate the pressure exerted by 2 dm $^3$  mol $^{-1}$  of ethane at 27°C if it follows van der Waal's equation  $a = 5.489 \text{ dm}^6 \text{ atm mol}^{-2}$ ,  $b = 0.0638 \text{ dm}^3 \text{ mol}^{-1}$ . Compare the value if the gas is ideal.

## Solution As

$$\left( P + \frac{n^2 a}{V^2} \right) \cdot (V - nb) = nRT$$

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$= \frac{0.0821 \times 300}{(2.0 - 0.0638)} - \frac{5.489}{(2)^2}$$

$$= 12.72 - 2.7445 = 9.976 \text{ atm}$$

From ideal gas equation

$$PV = RT$$

$$P = \frac{RT}{V} = \frac{0.0821 \times 300}{2}$$

$$= 12.315 \text{ atm}$$

33. The Van der Waal's constant ' $b$ ' for helium gas is 0.0237 litre mole $^{-1}$ . Calculate the approximately diameter of the helium molecule assuming the molecule to be spherical.

**Solution** As  $b = 4 N \frac{4}{3} \pi r^3$

$$\text{Here } b = 0.0237 \text{ litre mole}^{-1} = 23.7 \text{ ml mol}^{-1}$$

$$N = 6.02 \times 10^{23}$$

$$23.7 = 4 \times 6.02 \times 10^{23} \times \frac{4}{3} \times \frac{22}{7} \times r^3$$

$$r^3 = \frac{23.7 \times 21}{16 \times 6.02 \times 10^{23} \times 22}$$

On solving

$$r = 1.33 \times 10^{-8} \text{ cm.}$$

So the diameter of helium molecule is  $2.66 \times 10^{-8} \text{ cm}$ .

## Gas Analysis or Eudiometry

It is the process of gas analysis used to determine molecular formula percentage composition of gaseous mixture.

Gas eudiometry is based on Avogadro's law which states that "equal volume of all gases under similar conditions of temperature contain equal number of molecules or equal number of moles". It means volume ratio among gases is same as mole ratio at constant temperature and constant pressure.

During gas analysis, the eudiometer tube filled with mercury is inverted over a trough having mercury. A calculated volume of the gas or gaseous mixture is introduced, which displaces an equivalent

## 2.18 ■ Gaseous and Liquid States

amount of mercury. Now a known excess of oxygen is introduced and is electrically sparked, where by the combustible material gets oxidized. the volume of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  or other gaseous products of combustion are next determined by absorbing them in a suitable reagent. After each electric spark the reaction mixture is brought to the room conditions.

### Example,

$\text{O}_2$  : Alkaline pyrogallol

$\text{N}_2$  : Heated Mg

Acidic gases  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{X}_2$  :  $\text{NaOH}$  or  $\text{KOH}$  solution

Water vapour produced during the reaction can be determined by noting contraction in volume caused due to cooling.

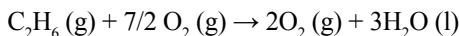
From this data we got some useful conclusions regarding gaseous reactions as follows:

- Composition of the gaseous mixture
- Molecular formula of gases
- Volume-volume relationship between gases

### Illustrations

34. When 100 ml sample of methane and ethane along with excess of  $\text{O}_2$  is subjected to electric spark, the contraction in volume was observed to be 212 ml. When the resulting gases were passed through KOH solution, further contraction in volume was?

**Solution**  $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$



Total contraction in volume

$$2\text{X} + 2.5(100 - \text{X}) = 212$$

$$2\text{X} - 2.5 \text{X} = 212 - 250$$

On solving, we get

$$\text{X} = 76$$

So contraction in volume when passed through KOH solution

= volume of  $\text{CO}_2$  evolved

$$= \text{X} + 2(100 - \text{X}) = 124 \text{ ml}$$

### LIQUID STATE

Liquids are characterized by the following properties.

- They have no definite shape but have definite volume.
- They have more density than gases but lower than solids.
- They have more compressibility than solids but less than gases as small voids are present between liquid molecules.
- They have slower diffusion rate than gases but more than solids due to small voids and slow molecular motion by liquids.
- The distance of separation between the molecules of a liquid is in the range  $10^{-7}$  to  $10^{-9}$  meter.
- The attraction and repulsion present between molecules of liquids can be explained by Lennard-Jones 6-12 potential model.
- H. Eyring and T. Ree introduced Hole theory or Vacancy theory of liquids.
- Liquids diffuse slowly as the molecules of liquids undergo large number of collisions with the neighbouring molecules.
- A liquid resembles a gas near critical temperature of the gas and with a solid near the m.p. of solid.

### Guldberg's Rule

According to it, normal boiling point ( $T_b$ ) of a liquid is nearly two third of its critical temperature ( $T_c$ ) when both the quantities are expressed on the absolute scale as follows:

$$T_b = \frac{2}{3} T_c$$

Here  $T_b$  = Boiling point

$T_c$  = Critical temperature

### Trouton's Law

According to it, in case of liquids having non-associated nature and not having very high boiling points, the ratio of the heat of vapourization to the normal boiling point of the liquid on the absolute scale is nearly equal to  $21 \text{ cal K}^{-1} \text{ mol}^{-1}$  or  $88 \text{ J K}^{-1} \text{ mol}^{-1}$ .

$$\frac{\Delta H_{\text{vap}}}{T_b} = 21 \text{ cal K}^{-1} \text{ mol}^{-1} \quad (\text{When } \Delta H_v \text{ is in cal})$$

or

$$\frac{\Delta H_{\text{vap}}}{T_b} = 88 \text{ J K}^{-1} \text{ mol}^{-1} \quad (\text{When } \Delta H_v \text{ is in J})$$

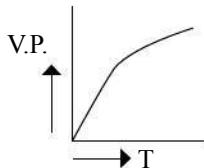
Here  $\Delta H_{\text{vap}}$  = Heat of vapourisation

$T_b$  = Boiling point of a liquid

## Vapour Pressure

At a particular temperature, it is the pressure exerted by vapours over liquid surface when vapours are in equilibrium with liquid.

- Vapour pressure increases with increase of temperature.



- The variation of vapour pressure of liquid with temperature is given as

$$\log P = -\frac{A}{T} + 1$$

Here A = Constant

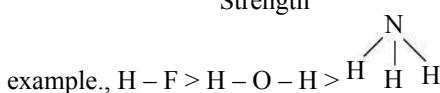
P = Vapour pressure of liquid

T = Temperature

- The plot of log P vs 1/T will be in a straight line.
- The vapour pressure of  $H_2O$  at 373 K is 76 cm.
- At critical temperature the meniscus between liquid and vapour disappears.
- Vapour pressure  $\propto$  Extent of H-bonding

or

Strength



- Heat of vaporization  $\propto$  H-bonding  
example,  $HF > H_2O > NH_3$
- The amount of heat needed to convert one gram of a liquid into its vapours at its B.P. is known as heat or enthalpy or latent heat of vaporization.
- **Clausius – Clapeyron Equation:** It explains the effect of temperature on vapour pressure of a liquid and also the effect of pressure on the boiling point of a liquid.

$$\log \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap.}}}{2.303} \cdot \frac{(T_2 - T_1)}{(T_1 \cdot T_2)}$$

## REMEMBER

- Formation of bubbles in a liquid in due to vapour pressure.
- Rate of evaporation does not change with time at a particular temperature however rate of condensation increases with time.
- At equilibrium rate of condensation and rate of evaporation are equal

## Difference Between Evaporation and Boiling Processes

- During evaporation cooling occurs as the average kinetic energy of the liquid decreases since molecules with higher kinetic energy leave the surface.
- Boiling occurs only at a specific temperature while evaporation can take place at any temperature.
- Boiling occurs below the surface while evaporation occurs only at surface.

## Surface Tension

It is the force at right angles to the surface of a liquid along one cm or one metre length of the surface.

- Units: Newton metre<sup>-1</sup> or [Nm<sup>-1</sup>], dyne cm<sup>-1</sup>.
- Due to surface tension the surface area of the liquid decreases upto minimum. example., Falling drops are spherical that is, minimum surface area for a given volume.
- Due to surface tension a liquid rises in capillary tube, water move upward in soil and walking of insects over water surface.
- Surface tension  $\propto$  1/Temperature.
- At critical temperature surface tension is zero.
- The effect of temperature is given by Eotvos equation.

$$\gamma = K (T_c - T) (d/M)^{2/3}$$

Here K = Constant

d = Density

M = Molar mass

**Measurement of Surface Tension:** To measure surface tension, Stalgmometer is used. It is based upon the fact that surface tension is directly proportional to the amount or weight of the spherical drop falling from the vertically kept capillary tube.

## 2.20 ■ Gaseous and Liquid States

$$\gamma \propto M \text{ so } \gamma_1/\gamma_2 = M_1/M_2.$$

**Surface Energy:** It is work in ergs needed to increase the surface area by 1 square centimetre. Its units are erg/cm<sup>2</sup> or Joule/metre<sup>2</sup>.

### REMEMBER

- Soap, detergent, alcohol, cholesterol are some surface active substances or surfactants which decrease surface tension.
- Due to force of adhesion water drops stick to a glass surface.

**Viscosity:** It is the internal resistance of a liquid to flow which exists due to the relative motion between two layers. It decreases with increase of temperature. It is calculated as the force per unit area needed to maintain a velocity difference of unity between two parallel layers of liquid unit distance apart.

**Viscosity Coefficient ( $\eta$ ):** It is the force of friction needed to maintain a velocity difference of 1 cm sec<sup>-1</sup> between any two parallel layers of 1 cm<sup>2</sup> area and which are 1 cm apart.

$$\eta = \frac{f \cdot x}{A \cdot v} = \frac{\text{dynes} \times \text{cm}}{\text{cm}^2 \times \text{cm sec}^{-1}} = \text{dyne cm}^{-2} \text{ sec}$$

$$= 1 \text{ poise}$$

Here  $f$  = Force

$a$  = Area

$v$  = Velocity difference

$x$  = Distance between two layers

$$1 \text{ Poise} = 1 \text{ gm cm}^{-1} \text{ sec}^{-1}$$

$$\text{Since dyne} = \text{gm} \times \text{cm} \times \text{sec}^{-2}$$

$$1 \text{ Poise} = 1/10 \text{ Newton metre}^2 \text{ sec}^{-1}$$

$$\text{or Pas or Kg m}^{-1} \text{ s}^{-1}$$

**Effect of Temperature on Viscosity:** On increasing temperature, viscosity decreases as average thermal energy of molecules increases hence the effect of intermolecular attraction forces decreases.

It can be shown by Arrhenius equation as follows:

$$\eta = A e^{E_a/RT}$$

Here  $T$  = Temperature

$R$  = Universal gas constant

$E_a$  = Activation energy

### Measurement of Viscosity:

- To measure viscosity Ostwald viscometer is used which is based on Poiseville's equation.

$$\eta = \frac{\pi P r^4 t}{8 V l}$$

Here 'V' volume of liquid needs time 't' to flow through a capillary tube of radius (r) and length 'l' under a pressure (P).

- When the same volume of two liquids say X and Y are flowing from the same height and through the same capillary then

$$\eta_X = \frac{\pi P_X r^4 t_X}{8 V l}$$

$$\eta_Y = \frac{\pi P_Y r^4 t_Y}{8 V l}$$

On dividing them

$$\frac{\eta_X}{\eta_Y} = \frac{P_X t_X}{P_Y t_Y}$$

$$\text{As } P = \eta d g$$

So

$$\frac{\eta_X}{\eta_Y} = \frac{d_X t_X}{d_Y t_Y}$$

$$\text{or } \eta_X = (d_X t_X / d_Y t_Y) \eta_Y$$

Here  $d_X$  = Density of liquid X

$d_Y$  = Density of liquid Y

$t_X$  = Time for flow of liquid X

$t_Y$  = Time for flow of liquid Y.

**Fluidity:** It is the reciprocal of viscosity coefficient of a liquid denoted by  $\phi$ .

$$\phi = \frac{1}{\eta}.$$

### REMEMBER

- In case of super fluid liquids, the resistance to flow becomes almost zero. It is called super fluidity.
- He at 2.18 K becomes super fluid liquid.
- Viscosity  $\propto$  H-bonding
- $\propto$  Molecular weight

Example, Glycerol > Glycol > Ethanol >  
 $\text{CH}_3\text{OH}$

### Enhance Your Knowledge

#### Critical Phenomenon and Liquefaction of Gases

##### Critical Temperature ( $T_c$ ):

It is the temperature above which the gas can not be liquefied with the help of high pressure also. It is denoted by  $T_c$ .

$$T_c = \frac{8a}{27Rb}$$

- Each gas has a definite critical temperature. E.g. 2  $T_c$  for  $\text{CO}_2$ ,  $\text{O}_2$  and  $\text{H}_2$  are  $31.1^\circ\text{C}$ ,  $118.8^\circ\text{C}$  and  $-240^\circ\text{C}$  respectively.

**Critical Volume ( $V_c$ ):** It is the volume occupied by one mole of the gas at critical temperature and critical pressure. It is denoted by  $V_c$ .

$$V_c = 3b$$

**Critical Pressure:** It is the minimum pressure required to liquefy any gas at critical temperature. It is denoted by  $P_c$ .

$$P_c = \frac{a}{27 b^2}$$

#### Relation Between $T_c$ , $V_c$ and $P_c$

$$P_c V_c = 3/8 R T_c$$

**Liquefaction of Gases:** A gas can be liquefied by decrease in temperature or increase in pressure. When a gas is compressed at any temperature the intermolecular distance decreases as a result intermolecular forces become effective and decreases kinetic energy this cause liquefaction.

liquefaction  $\propto$  'a' (Intermolecular force)

### Methods of Liquefaction of Gases

- (1) Linde's process, By adiabatic expansion of compressed gas that is, Joule – Thomson effect.
- (2) Claude's process, By adiabatic expansion of compressed gas involving mechanical work.
- (3) Through adiabatic demagnetization.
- (4) Cooling by freezing mixtures. Example,  $\text{NaCl}$  and ice (251 K),  $\text{CaCl}_2$  and ice (218 K)

**Boyle's Temperature:** It is the temperature at which real gases obey gas laws or The temperature above which the gases behave like an ideal gas. It is denoted by  $T_b$ .

$$T_b = \frac{a}{R_b}$$

Easily liquefiable gases have high value of  $T_b$ . example.,  $T_b$  of  $\text{O}_2$  is 40 K.

**Inversion Temperature ( $T_i$ ):** It is the temperature at which a gas shows neither cooling nor heating effect in Joule-Thomson adiabatic expansion. ( $\mu_{J,T} = 0$ )

- Below inversion temperature cooling effect occurs. ( $\mu_{J,T} = -ve$ )
- Above inversion temperature heating effect occurs ( $\mu_{J,T} = +ve$ )

$$T_i = \frac{2a}{Rb}$$

**Relative Humidity ( $R_h$ ):** It represents the ratio of the mass of water vapours (m) actually present in a definite volume of air at room temperature to the maximum mass of water vapours (M) needed to saturated the same volume at the same temperature.

$$R_h = m/M$$

$$= \frac{\text{Vapour pressure of water or gas}}{\text{Saturated vapour pressure}}$$

(As vapour pressure  $\propto$  mass)

### REMEMBER

As at dew point a gas becomes saturated so vapour pressure of  $\text{H}_2\text{O}$  at room temperature is equal to saturated vapour pressure of water at dew point.

$$R_h =$$

$$\frac{\text{Saturated vapour pressure at dew point}}{\text{Saturated vapour pressure at room temperature}}$$

### REMEMBER

- The order of kinetic energy is solid < liquid < gas.
- Kinetic energy at absolute zero temperature is zero.
- Boyle's Law according to kinetic theory:  

$$PV = \frac{1}{2} MV^2 \text{ r.m.s}$$
- Charle's Law according to kinetic theory:  

$$V = (\text{M}/3\text{P}) V^2 \text{ r.m.s}$$
- **Gay Lussac Law**  

$$P = (\text{M}/3V) V^2 \text{ r.m.s}$$
- **Loschmidt Number:** It is the number of molecules present in 1 cm<sup>3</sup> of a gas or vapour at S.T.P (value =  $2.7678 \times 10^{19}$  per c.c)
- At constant P,  $V/T = \text{constant}$ , hence plot of V versus T is linear passing through the origin
- Gas constant is work done per degree per moles.
- Saturated vapours do not obey gas laws except Dalton's law as their pressure is independent of volume.

- Saturated vapours do not obey gas laws except Dalton's law as their pressure is independent of volume. Aqueous tension depends only on temperature.
- With increase in temperature most probable velocity increases but the fraction possessing it decreases.
- Hydrogen and helium show heating effect on adiabatic expansion (Joule–Thomson effect) because their inversion temperatures are low.
- $C_p - C_v = R$  for 1 mole of an ideal gas.
- A thermometer used only for the measurement of small differences in temperature like depression in freezing point etc. is Beckmann thermometer.
- **Escape Velocity (V<sub>e</sub>):** It is the minimum velocity needed by an object to escape from the gravitational field of the body.

$$V_e = \sqrt{2gr}$$

### Solved Problems from the IITs

1. At 27°C, hydrogen is leaked through a tiny hole into a vessel for 20 minutes. Another unknown gas at the same temperature and pressure as that of H<sub>2</sub> is leaked through the same hole for 20 minutes. After the effusion of the gases, the mixture exerts a pressure of 6 atmosphere. The hydrogen content of the mixture is 0.7 mole. If the volume of the container is 3 litres, what is the molecular weight of the unknown gas?

[IIT/JEE 1992]

**Solution** Let P<sub>H<sub>2</sub></sub> and p be the partial pressures of hydrogen and unknown gas respectively and w be the number of moles of unknown gas.

$$P_{H_2} = \frac{0.7}{3} \times 0.0821 \times 300 \quad \dots \text{(i)}$$

$$p(\text{unknown}) = \frac{w}{3} \times 0.0821 \times 300 \quad \dots \text{(ii)}$$

By adding equation (i) and (ii), we get

$$P_{H_2} + p = 6 = \frac{1}{3} \times 0.0821 \times 300 (0.7 + w)$$

On solving, we get

$$w = 0.0308 \text{ mole}$$

According to law of diffusion,

$$\frac{0.7/20}{0.0308/20} = \sqrt{(M/2)}$$

$$M = 1033$$

2. A gas bulb of 1 litre capacity contains  $2.0 \times 10^{21}$  molecules of nitrogen exerting a pressure of  $7.57 \times 10^3 \text{ N m}^{-2}$ . Calculate the root mean square (r.m.s) speed and the temperature of the gas molecules. If the ratio of the most probable speed to the root mean square speed is 0.82, calculate the most probable speed for these molecules at this temperature.

[IIT 1993]

**Solution** Amount of gas =  $\frac{2.0 \times 1021}{6.023 \times 1023}$  mole

$$\text{As } Pv = nRT$$

$$T = \frac{PV}{nR}$$

$$T = \frac{10^{-3} \times 7.57 \times 10^3}{2.0 \times 10^{21} \times 8.314} = 274.2 \text{ K}$$

$$6.023 \times 10^{-23}$$

$$\text{RMS speed} = \sqrt{(3RT/M)}$$

$$= \frac{\sqrt{(3 \times 8.314 \times 274.2)}}{\sqrt{(28 \times 10^{-3})}}$$

$$= 494.22 \text{ ms}^{-1}$$

$$\text{Most probable speed} = 0.8 \times \text{RMS}$$

$$= 0.8 \times 494.22 \text{ ms}^{-1}$$

$$= 395.376 \text{ ms}^{-1}$$

3. A 4 : 1 molar mixture of He and CH<sup>4</sup> is contained in a vessel at 20 bar pressure. Due to a hole in the vessel the gas mixture leaks out. What is the composition of the mixture effusing out initially?

[IIT 1994]

$$\text{Rate of effusion} = K \cdot \frac{P}{\sqrt{M}}.$$

Here P is partial pressure of the gas

M = Molar mass, M of He = 4,

M of CH<sup>4</sup> = 16

$$\frac{\text{Rate of effusion of He}}{\text{Rate of effusion of CH}_4} = \frac{K P_{\text{He}} \sqrt{M_{\text{He}}}}{K P_{\text{CH}_4} \sqrt{M_{\text{CH}_4}}}$$

$$= \frac{P_{\text{He}}}{P_{\text{CH}_4}} \times \sqrt{\left(\frac{M_{\text{CH}_4}}{M_{\text{He}}}\right)}$$

$$= \frac{4}{1} \sqrt{(16/4)} = 8$$

4. The composition of the equilibrium mixture (Cl<sub>2</sub>  $\leftrightarrow$  2Cl), which is attained at 1200°C, is determined by measuring the rate of effusion through a pinhole. It is observed that at 1.80 mm Hg pressure, the mixture effuses 1.16 times as fast as Krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms. (Atomic wt. of Kr = 84)

[IIT 1995]

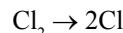
**Solution** According to Graham's law of diffusion

$$\frac{r_{\text{mix}}}{r_K} = \sqrt{\left(\frac{M_K}{M_{\text{Mix}}}\right)}$$

$$\text{that is, } 1.16 = \sqrt{\left(\frac{84}{M}\right)} (\text{As } P_1 = P_2)$$

On solving

$$M = 62.425$$



$$1 \quad 0 \quad \text{Initially}$$

$$(1 - \alpha) \quad 2\alpha \quad \text{at equilibrium}$$

$$\frac{\text{Normal molecular weight}}{\text{Exp. Molecular weight}} = 1 + \alpha$$

$$\frac{71}{62.425} = 1 + \alpha$$

$$\text{So } \alpha = 0.1374 = 13.7\%$$

5. One way of writing the equation of state for real gases is

$$PV = RT [1 + B/V + \dots]$$

where B is a constant. Derive an approximate expression for B in terms of van der Waal's constants a and b.

[IIT 1997]

**Solution**  $[P + \frac{a}{V^2}] [V - b] = RT$

$$P = \frac{RT}{(V - b)} - \frac{a}{V^2}.$$

If we multiply it by V then

$$PV = \frac{RTV}{(V - b)} - \frac{a}{V}.$$

$$= RT \left[ \frac{V}{V - b} - \frac{a}{VRT} \right]$$

$$= RT \left[ \left( \frac{1 - b}{V} \right)^{-1} - \frac{a}{VRT} \right]$$

As

$$\left[ 1 - \frac{b}{V} \right]^{-1} = 1 + \frac{b}{V} + \left( \frac{b}{V} \right)^2 + \dots$$

$$PV = RT \left[ 1 + \frac{b}{V} + \dots - \frac{a}{VRT} \right]$$

$$PV = RT \left[ 1 + \left( b - \frac{a}{RT} \right) \cdot \frac{1}{V} + \dots \right]$$

$$B = b - \frac{a}{RT}.$$

6. Using van der Waal's equation, calculate the constant 'a' when two moles of a gas confined in a four litre flask exerts a pressure of 11.0 atm

## 2.24 ■ Gaseous and Liquid States

spheres at a temperature of 300 K. The value of 'b' is 0.05 lit.mol<sup>-1</sup>.

[IIT 1998]

**Solution** For n moles of a gas

$$\left( P + n^2 \frac{a}{V^2} \right) (V - nb) = nRT$$

$$[1 + (2^2 a / 4^2)] [4 - 2 \times 0.05] = 2 \times 0.082 \times 300$$

$$a = 6.46 \text{ atm litre}^2 \text{ mol}^{-2}$$

7. An evacuated glass vessel weighs 50.0 g when empty, 148.0 g when filled with a liquid of density 0.98 g mL<sup>-1</sup> and 50.5 g when filled with an ideal gas at 760 mm Hg at 300K. Determine the molecular weight of the gas.

[IIT 1998]

**Solution** Van der Waal's equation for n mole of gas is given as:

$$\left[ P + \frac{n^2 a}{V^2} \right] (V - nb) = nRT$$

Here V = 4 litre, P = 11.0 atm, T = 300 K,

b = 0.05 litre mol<sup>-1</sup>, n = 2

$$[11 + \frac{(2)^2 a}{(4)^2}] [4 - 2 \times 0.05] = 2 \times 0.082 \times 300$$

$$a = 6.46 \text{ atm litre}^2 \text{ mol}^{-2}$$

8. One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 s to diffuse through the same hole. Calculate the molecular formula of the compound.

[IIT 1999]

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2/M_1}{P_2}} \times \frac{P_1}{P_2}$$

$$\frac{t_1}{t_2} \times \frac{t_2}{n_2} = \sqrt{\frac{M_2/M_1}{P_2}} \times \frac{P_1}{P_2}$$

$$\frac{1}{38} \times \frac{57}{1} = \sqrt{\frac{Mg/28}{1.6}} \times \frac{0.8}{1.6}$$

$$Mg = (57/38 \times 1.6/0.8)2 \times 28$$

On solving

$$Mg = 252$$

Thus, compound is XeF<sub>6</sub> because it can have only one xenon atom.

9. One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 s to diffuse through the same hole. Calculate the molecular formula of the compound.

[IIT 1999]

**Solution** Apply Graham's law of diffusion

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2/M_1}{P_2}} \times \frac{P_1}{P_2}$$

$$\text{As } r = n/t$$

$$\frac{n_1}{t_1} \times \frac{t_2}{n_2} = \sqrt{\frac{M_2/M_1}{P_2}} \times \frac{P_1}{P_2}$$

$$\frac{1}{38} \times \frac{57}{1} = \sqrt{\frac{Mg/28}{1.6}} \times \frac{0.8}{1.6}$$

On squaring both sides

$$Mg = [\frac{57}{38} \times \frac{1.6}{0.8}]^2 \times 28$$

$$Mg = 252$$

So compound may be XeF<sub>6</sub> because it can have only one xenon atom (since for two xenon atoms, 2 × atomic weight of Xe = 2 × 131 = 262) i.e., greater than 252

$$\begin{aligned} \text{XeF}_6 &= 131 + 6 \times 19 \\ &= 131 + 114 \\ &= 245 \end{aligned}$$

10. The pressure exerted by 12 g of an ideal gas at temperature t°C in a vessel of volume V litre is one atm. When the temperature is increased by 10 degrees at the same volume, the pressure increases by 10 %. Calculate the temperature t and volume V (mol. weight of the gas = 120).

[IIT 1999]

At constant volume, pressure law is used

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}$$

$$\frac{1}{1.1} = \frac{t + 273}{t + 283}$$

$$t = -173^\circ\text{C} = 100 \text{ K}$$

Now according to gas equation

$$PV = nRT$$

$$V = \frac{n}{P} RT$$

$$= \frac{12 \times 0.082 \times 100}{120 \times 1}$$

= 0.82 litre

11. (a) Calculate the pressure exerted by 5 mole of  $\text{CO}_2$  in one litre vessel at  $47^\circ\text{C}$  using van der Waal's equation. Also report the pressure of gas if it behaves ideally in nature. Given that  $a = 3.592 \text{ atm litre}^2 \text{ mol}^{-2}$ ,  $b = 0.0427 \text{ litre mol}^{-1}$ .

(b) If volume occupied by  $\text{CO}_2$  molecules is negligible, then calculate the pressure exerted by one mole of  $\text{CO}_2$  gas at 273 K.

[IIT 2000]

**Solution** According to van der Waal's equation for  $n$  mole

$$[P + \frac{n^2 a}{V^2}] [V - nb] = nRT$$

$$[P + \frac{25 \times 3.592}{1}] [1 - 5 \times 0.0427]$$

$$= 5 \times 0.0821 \times 320$$

On solving

$$P = 77.218 \text{ atm}$$

Also it gas behaves ideally, then  $PV = nRT$

$$P \times 1 = 5 \times 0.0821 \times 320$$

$$= 131.36 \text{ atm}$$

For 1 mole

$$[P + \frac{a}{V^2}] [V - b] = RT$$

If  $b$  is negligible we can use

$$P = \frac{RT}{V} - \frac{a}{V^2}$$

that is,  $PV^2 - RTV + a = 0$

$$\text{or } V = \frac{+ RT \pm \sqrt{(-RT)^2 - 4Pa}}{2P}$$

At given  $P$  and  $T$ ,  $V$  has only one value and thus discriminant = 0

$$\text{So } (RT)^2 - 4Pa = 0$$

$$\text{or } P = \frac{R^2 T^2}{4a}$$

$$= \frac{(0.082)^2 \times (273)^2}{4 \times 3.592}$$

$$= 34.88 \text{ atm}$$

12. The compression factor (compressibility factor) for 1 mole of a van der Waal's gas at  $0^\circ\text{C}$  and 100 atmospheric pressure is found to be 0.5. Assuming that the volume of gas molecule is negligible calculate the van der Waal's constant 'a'.

[IIT 2001]

**Solution** As  $Z = \frac{PV}{RT} = 0.5$

$$\text{So } \frac{100 \times V}{0.082 \times 273} = 0.5$$

On solving

$$V = 0.112 \text{ litre}$$

Now applying van der Waal's equation

$$[P + \frac{a}{V^2}] [V - b] = bT$$

As  $b$  is negligible)

$$[P + \frac{a}{V^2}] = \frac{RT}{V}$$

$$[100 + \frac{a}{(0.112)^2}] = \frac{0.082 \times 273}{0.112}$$

$$= 199.88$$

$$\frac{a}{(0.112)^2} = 99.88$$

$$a = 1.253 \text{ litre}^2 \text{ mol}^2 \text{ atm.}$$

13. The density of the vapours of a substance at 1 atm pressure and 500 K is  $0.36 \text{ kg m}^{-3}$ . The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same conditions?

- (a) Determine (i) molecular weight, (ii) molar volume (iii) compression factor ( $Z$ ) of the vapours and (iv) which forces among gas molecules are dominating, the attractive or the repulsive?
- (b) If the vapours behave ideally at 1000 K, determine the average translational kinetic energy of a molecule.

[IIT 2002]

**Solution** According to Graham's law of diffusion

(a)

$$(i) \frac{r}{r_{O_2}} = \sqrt{\left(\frac{M_{O_2}}{M_v}\right)}$$

$$1.33 = \sqrt{\left(\frac{32}{M_v}\right)}$$

On solving

$$M_v = 18.1$$

## 2.26 ■ Gaseous and Liquid States

(ii) Molar volume at 500 K

$$= \frac{\text{Molecular weight}}{\text{Density of one mole}}$$

$$= \frac{18.1 \times 10^{-3}}{0.36}$$

$$= 50.25 \times 10^{-3} \text{ m}^3$$

$$\text{(iii) Compression factor } (Z) = \frac{PV}{RT}$$

$$= \frac{101325 \times 50.25 \times 10^{-3}}{8.314 \times 500}$$

$$= 1.225$$

(iv) Repulsive forces operates among molecules as  $Z > 1$ .

$$\text{(b) Average K.E.} = \frac{3}{2} \frac{RT}{N} = \frac{3}{2} KT$$

$$= \frac{3}{2} \times 1.38 \times 10^{-23} \times 1000$$

$$= 2.07 \times 10^{-20} \text{ J}$$

14. The average velocity of gas molecules is 400 m/sec. Calculate its rms velocity at the same temperature.

[IIT 2003]

**Solution** Average velocity are given as

$$V_{AV} = \sqrt{(8RT/\pi M)} \quad \dots \text{(i)}$$

$$V_{rms} = \sqrt{(3RT/M)} \quad \dots \text{(ii)}$$

Now divide equation (ii) by (i)

$$V_{rms}/V_{AV} = \sqrt{(3\pi/8)}$$

As  $V_{AV} = 400 \text{ m/sec.}$

$$V_{rms} = \sqrt{(3 \times 31.4/8)} \times V_{AV}$$

$$= \sqrt{(3 \times 3.14/8)} \times 400$$

$$= 434 \text{ m/sec}$$

15.  $C_v$  value of He is always  $3R/2$  but  $C_v$  value of  $H_2$  is  $3R/2$  at low temperature and  $5R/2$  at moderate temperature and more than  $5R/2$  at higher temperature. Explain.

[IIT 2003]

**Solution** As we know that heat absorbed is used in increasing kinetic energy, rotational energy and vibrational energy of molecules.

- (i) As helium is monoatomic so heat given is used to increase its kinetic energy ( $= 3RT/2$ ) only and hence

$$C_v = \frac{3R}{2}.$$

- (ii) As  $H_2$  is diatomic and at low temperature heat given is used in increasing its kinetic energy

$$\text{that is, } C_v = \frac{3R}{2}.$$

- (iii) At moderate temperature, heat given is used to increase both kinetic and rotational energies

$$(= \frac{3RT}{2} + RT) \text{ and } C_v = \frac{5R}{2}.$$

- (iv) At high temperature, heat given is used to increase all the kinetic, rotational and vibrational energies and hence

$$C_v > \frac{5R}{2}.$$

16. For a real gas obeying van der Waal's equation, a graph is plotted between  $PV_m$  (y-axis) and  $P(x\text{-axis})$  where  $V_m$  is molar volume. Find y-intercept of the graph.

[IIT Mains 2004]

**Solution** At very low pressure the Van der Waal's equation reduces to ideal gas equation.

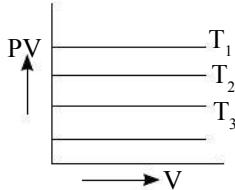
that is,  $PV = nRT$

$$PV_m = RT \text{ (for 1 mole of the gas)}$$

Hence y-intercept of the graph =  $RT$ .

## MULTIPLE-CHOICE QUESTIONS

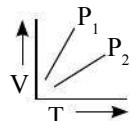
### Straight Objective Type Questions (Single Choice only)

1. The correct equation for Boyle's law is
  - a.  $\frac{d^2P}{P} = -\frac{dV}{dT}$
  - b.  $\frac{d^2P}{P} = +\frac{d^2V}{dT^2}$
  - c.  $\frac{dP}{P} = -\frac{dV}{V}$
  - d.  $\frac{dP}{P} = +\frac{dV}{V}$
2. Under which of the following conditions, Van der Waal's gas approaches ideal behaviour?
  - a. Extremely low pressure
  - b. High pressure
  - c. Low product of PV
  - d. Low temperature
3. Slope of the plot between PV and P at constant temperature is
  - a.  $\frac{1}{2}$
  - b. 1
  - c. Zero
  - d.  $1/\sqrt{2}$
4. Molar volume of  $\text{CO}_2$  is maximum at
  - a.  $0^\circ\text{C}$  and 2.0 atm
  - b. N.T.P.
  - c.  $273^\circ\text{C}$  and 2 atm
  - d.  $127^\circ\text{C}$  and 1 atm
5. Consider the graph given below and select the correct choice:
 

**T<sub>1</sub>**      **T<sub>2</sub>**      **T<sub>3</sub>**

  - a.  $T_1 > T_2 > T_3$
  - b.  $T_1 < T_2 < T_3$
  - c.  $T_1 = T_2 = T_3$
  - d.  $T_1 = T_2 > T_3$

6. V vs T curves at constant pressure  $P_1$  and  $P_2$  for an ideal gas are shown below.



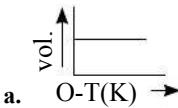
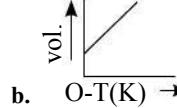
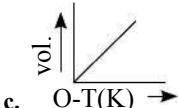
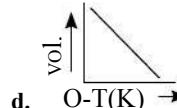
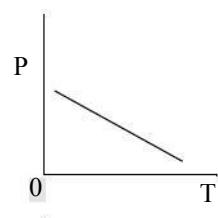
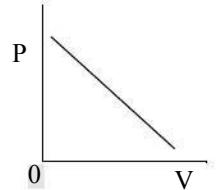
Which of these is correct?

- a.  $P_1 > P_2$
- b.  $P_1 < P_2$
- c.  $P_1 = P_2$
- d. All of above

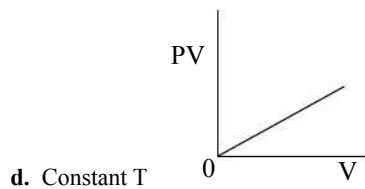
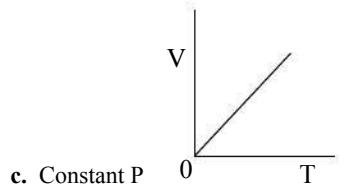
7. In an open end manometer, one end of a U-tube filled with mercury is attached to a gas-filled container and the other end is open to the atmosphere. If the gas pressure in the container is less than atmospheric pressure
  - a. The Hg level will be higher in the arm open to the atmosphere
  - b. Hg will be forced out of the open end of the U-tube.
  - c. The difference between the Hg levels in the two arms will be greater than 76 cm.
  - d. The Hg level will be higher in the arm connected to the container.
8. A gas behaves like an ideal gas under conditions of
  - a. high pressure and low temperature
  - b. high temperature and high pressure
  - c. low pressure and high temperature
  - d. low pressure and low temperature.
9. Suppose one needs to closely monitor small changes in pressure inside a container using an open end manometer. For the best accuracy, the substance in the manometer should
  - a. be mercury
  - b. have a low density
  - c. have a high density
  - d. be a solid
10. When the temperature is raised, the viscosity of the liquid decreases. This is because
  - a. Attraction between the molecules increases
  - b. Covalent and hydrogen bond forces decrease
  - c. Volume of the solution decreases
  - d. Increase in temperature increases the average kinetic energy of the molecules which overcomes the attractive force between them
11. At constant volume and temperature conditions the rates of diffusion  $D_A$  and  $D_B$  of gases A and B having densities  $\rho_A$  and  $\rho_B$  are related by the expression
  - a.  $D_A = [D_B \rho_A / \rho_B]^{1/2}$
  - b.  $D_A = [D_B \rho_B / \rho_A]^{1/2}$
  - c.  $D_A = D_B [\rho_A / \rho_B]^{1/2}$
  - d.  $D_A = D_B [\rho_B / \rho_A]^{1/2}$

## 2.28 ■ Gaseous and Liquid States

12. Which of the following gases has the lowest average speed at 25°C?
- $\text{NH}_3$
  - $\text{O}_2$
  - $\text{CH}_4$
  - $\text{H}_2\text{S}$
13. If the four tubes of a car are filled to the same pressure with  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2$  and  $\text{Ne}$  separately, then which one will be filled first?
- $\text{O}_2$
  - $\text{H}_2$
  - $\text{Ne}$
  - $\text{N}_2$
14. At constant volume for a fixed number of moles of a gas, the pressure of the gas increases with the rise in temperature due to
- increase in average molecular speed
  - increase in rate of collisions
  - increase in molecular attraction
  - increase in mean free path.
15. Which curve does not represent Boyle's law?
- 
16. An ideal gas expands according to  $PV = \text{constant}$ . On expansion, the temperature of gas
- will rise
  - will drop
  - will remain constant
  - cannot be determined because the external pressure is not known
17. For which of the following parameters, the structural isomers  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CH}_3\text{OCH}_3$  would be expected to have the same values? (assume ideal behaviour)
- Gaseous densities at the same temperature and pressure
  - Heat of vapourization
  - Boiling points
  - Vapour pressure at the same temperature
18. Which of the following has maximum root mean square velocity at the same temperature?
- $\text{H}_2$
  - $\text{O}_2$
  - $\text{SO}_2$
  - $\text{CO}_2$
19. The density of neon will be highest at
- STP
  - $0^\circ\text{C}$ , 2 atm
  - $273^\circ\text{C}$ , 1 atm
  - $273^\circ\text{C}$ , 2 atm
20. When the temperature of an ideal gas is increased from  $27^\circ\text{C}$  to  $927^\circ\text{C}$ , the kinetic energy will be
- same
  - eight times
  - four times
  - twice
21. The values of van der Waal's constant ' $\alpha$ ' for the gases  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{NH}_3$  and  $\text{CH}_4$  are 1.360, 1.390, 4.170 and  $2.253 \text{ L atm. mol}^{-2}$  respectively. The gas which can most easily be liquefied is
- $\text{O}_2$
  - $\text{N}_2$
  - $\text{NH}_3$
  - $\text{CH}_4$
22. Some assumptions from the kinetic molecular theory are listed below. Which one is most frequently cited to explain Charles's law?
- Collisions of gas particles are elastic and total kinetic energy of the gas is constant
  - A gas consists of tiny particles moving in random straight line motion.
  - The volume of the particles is negligible compared to the volume of the gas.
  - The average kinetic energy of gas articles is proportional to the Kelvin temperature.
23. Universal gas constant ( $R$ ) is divided by Avogadro's number ( $N_0$ ) then the value is equivalent to
- van der Waal's constant
  - Rydberg's constant
  - Planck's constant
  - Boltzmann's constant
24. The term that accounts for intermolecular force in van der Waal's equation for non ideal gas is
- $RT$
  - $V - b$
  - $(P + \alpha/V^2)$
  - $(RT)^{-1}$
25. According to the kinetic theory of gases, in an ideal gas, between two successive collisions a gas molecules travels
- in a circular path
  - in a wavy path

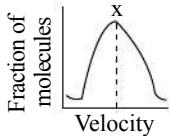
- c. in a straight line path  
d. with an accelerated velocity
26. Helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a helium atom is  
 a. same as that of a hydrogen molecule  
 b. half that of a hydrogen molecule  
 c. two times that of a hydrogen molecule  
 d. four times that of a hydrogen molecule
27.  $a/V^2$  given in van der Waal's equation is for  
 a. internal pressure  
 b. intermolecular attraction  
 c. Both (a) and (b)  
 d. temperature correction
28. Kinetic theory of gases presumes that collision between the molecules to be perfectly elastic because  
 a. the molecules are rigid  
 b. the molecules are tiny  
 c. the temperature remains constant irrespective of collision  
 d. collision will not split the molecules
29. The temperature at which real gases obey the ideal gas laws over a wide range of pressure is called  
 a. Critical temperature  
 b. Boyle temperature  
 c. Inversion temperature  
 d. reduced temperature
30. The correct representation of Charle's law is given in
- a.  b. 
- c.  d. 
31. 0.1 mole of gas absorbs 41.75 J of heat, the rise in temperature occurs 20°C, the gas must be  
 a. triatomic                      b. diatomic  
 c. monoatomic                    d. Both b. and c.
32. Which pair of the gases diffuses with the same rate at same temperature and pressure?
- a. CO and NO                    b.  $\text{NO}_2$  and  $\text{CO}_2$   
 c.  $\text{NH}_3$  and  $\text{PH}_3$                 d. NO and  $\text{C}_2\text{H}_6$
33. A real gas at a very high pressure occupies  
 a. Less volume than that of an ideal gas under identical conditions  
 b. More volume than that of an ideal gas under identical conditions  
 c. Same volume than that of an ideal gas under identical conditions  
 d. Cannot be predicted
34. Which one of the following, is van der Waal's equation, describing the behaviour of one mole of a real gas over wide ranges of temperature and pressure  
 a.  $(P + a/V^2)(V + b) = RT$   
 b.  $(P + a/V^2)(V - b) = RT$   
 c.  $(P - a/V^2)(V - b) = RT$   
 d.  $(P + a/V^2)(V - b) = R/T$
35. You are given two flasks of equal volume. One contains  $\text{H}_2$  at 0°C and 1 atm while the other contains  $\text{CO}_2$  at 0°C and 2 atm. which of the following quantities will be the same for both flasks?  
 a. Density  
 b. Number of molecules present  
 c. Average molecular speed  
 d. Average molecular kinetic energy
36. Temperature according to kinetic theory, is a measure of  
 a. Average translational kinetic energy of gas molecules  
 b. Intermolecular attraction  
 c. Intermolecular distances  
 d. Volume of gas
37. Which of the following diagrams correctly describes the behaviour of a fixed mass of an ideal gas? (T is measured in K).
- a. 
- b. 

## 2.30 ■ Gaseous and Liquid States



38. Which of the following gases has the highest average speed at 400 K?
- $\text{SF}_6$
  - $\text{UF}_6$
  - $\text{CO}_2$
  - $\text{N}_2\text{O}_4$

39. Distribution of fraction of molecules with velocity is represented in the figure



Velocity corresponding to point X is

- $\sqrt{2RT/M}$
- $\sqrt{3RT/M}$
- $\sqrt{8RT/\pi M}$
- none

40. Which of the following represents total kinetic energy of one mole of gas?
- $2/3 RT$
  - $3/2 RT$
  - $1/2 RT$
  - $(C_p - C_v) RT$

41. An unknown gas effuses 2.3 times faster than  $\text{N}_2\text{O}_4$  at the same temperature. What is the identity of the unknown gas?

- $\text{O}_3$
- $\text{N}_2\text{O}$
- $\text{NH}_3$
- $\text{CN}_2$

42. If  $V$  is the volume of one molecule of gas under given conditions, the van der Waal's constant 'b' is

- $4V$
- $4VN_0$
- $\frac{N_0}{4V}$
- $\frac{4V}{N_0}$

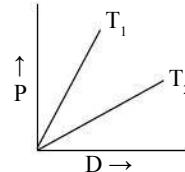
43. A gas deviates from ideal behaviour at a high pressure because its molecules

- Show the Tyndall effect
- Have kinetic energy
- Attract one another
- Are bound by covalent bonds

44. In van der Waal's equation of state of the gas law, the constant 'b' is a measure of

- intermolecular attraction
- intermolecular repulsions
- intermolecular collision per unit volume
- volume occupied by the molecules

45. Pressure vs density curve for an ideal gas at two different temperatures  $T_1$  and  $T_2$  is shown below. Which is correct relation here?



Which of these is correct?

- $T_1 > T_2$
- $T_1 < T_2$
- $T_1 = T_2$
- can not be said

46. Which statement about real gases is true?

- Forces of attraction and repulsion exist between gas particles at close range.
- The behaviour of real gases can be exactly predicted using the ideal gas law.
- The volume of the gas particles is zero.
- The mass of the gas particles is zero.

47. If  $\alpha$  is the volume coefficient of expansion and  $\beta$  is the compressibility coefficient of an ideal gas,  $\alpha/\beta$  is

- $T/P$
- $VR$
- $RT$
- $P/T$

48. The ratio  $a/b$  ( $a$  and  $b$  being the van der Waal's constant of real gases) has the dimensions of

- $\text{L mol}^{-1}$
- $\text{atm mol}^{-1}$
- $\text{atm L mol}^{-2}$
- $\text{atm L mol}^{-1}$

49. A perfect gas of a given mass is heated first in a small vessel and then in a large vessel, such that their volume remains unchanged. The  $P-T$  curves are:

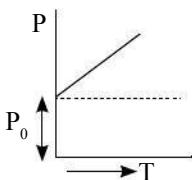
- Linear with same slope
- Linear with different slope
- Parabolic with same curvature
- Parabolic with different curvature

50. It is easier to liquefy oxygen than hydrogen because

- Oxygen has a higher critical temperature and a higher inversion temperature than hydrogen
- The critical temperature and inversion temperature of oxygen is very low
- Oxygen has a higher critical temperature and lower inversion temperature than hydrogen
- Oxygen has a lower critical temperature and higher inversion temperature than hydrogen

### Brainteaser Objective Type Questions (Single choice only)

51. Consider the figure given below and find the value of slope.

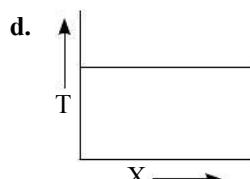
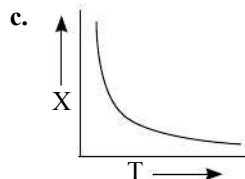
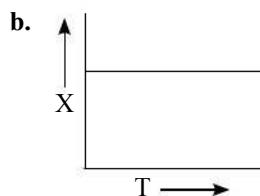
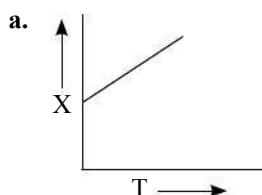


- a. Slope =  $(\partial T / \partial P)_V$
  - b. Slope =  $(\partial P / \partial T)_V$
  - c. Slope =  $(\partial V / \partial T)_P$
  - d. Slope =  $(\partial P / \partial T)_P$
52. X ml of  $H_2$  has effuse through a hole in a container in 5 seconds. The time taken for the effusion of the same volume of the gas specified below under identical conditions is
- a. 10 seconds : He
  - b. 20 seconds :  $O_2$
  - c. 25 seconds : CO
  - d. 55 seconds :  $CO_2$
53. 0.5 mole of each of  $H_2$ ,  $SO_2$  and  $CH_4$  are kept in a container. A hole was made in the container. After 3 hours, the order of partial pressures in the container will be
- a.  $p(CH_4) > p(SO_2) > p(H_2)$
  - b.  $p(H_2) > p(CH_4) > p(SO_2)$
  - c.  $p(SO_2) > p(CH_4) > p(H_2)$
  - d.  $p(H_2) > p(SO_2) > p(CH_4)$
54. Van der Waal's equation for a real gas is

$$(P + \frac{n^2 a}{V^2})(V - nb) = nRT$$

$$\text{Plot of quantity } X = \frac{ab}{a+b}$$

with temperature is



55. Which of the following statement(s) is (are) correct
- 1. A plot of  $\log K_p$  versus  $1/T$  is linear
  - 2. A plot of  $\log (X)$  versus time is linear for a first order reaction  $X \rightarrow P$
  - 3. A plot of  $\log P$  versus  $1/T$  is linear at constant volume
  - 4. A plot of  $P$  versus  $1/V$  is linear at constant temperature.
- a. 1, 2
  - b. 2, 4
  - c. 2, 3
  - d. 1, 4
56. The ratio between the root mean square velocity of  $H_2$  at 50 K and that of  $O_2$  at 800 K is.
- a. 4
  - b. 2
  - c. 1
  - d.  $\frac{1}{4}$
57. Consider the following statement(s) for viscosity ( $\eta$ ) variation with T and P for an ideal gas and select the incorrect statement
- 1.  $\eta$  of a gas increases with increase in both T and P
  - 2.  $\eta$  of a gas is independent of temperature and pressure
  - 3.  $\eta$  of a gas decreases with increase in T and increase with increase in P
  - 4.  $\eta$  of a gas increases with increase in temperature (T), but it is independent of pressure.
- a. 1 and 3
  - b. 2 and 3
  - c. 1, 2 and 3
  - d. 2, 3 and 4

## 2.32 ■ Gaseous and Liquid States

58. Equal weights of ethane and hydrogen are mixed in an empty container at 25°C. The fraction to total pressure exerted by hydrogen is
- 1:2
  - 1:1
  - 1:16
  - 15:16
59. A closed vessel contains equal number of molecules of O<sub>2</sub> and H<sub>2</sub>. Consider the following statements:
- The average speed of hydrogen molecules will be greater.
  - Weight of hydrogen is 1/8<sup>th</sup> of the weight of oxygen.
  - Hydrogen molecules strike the walls more often.
  - The two gases have different average energies.
- The statements are wrong in
- 2 and 4
  - 2 and 3
  - 1 and 4
  - 1 and 3
60. The rate of diffusion of methane at a given temperature is twice that of a gas X. The molecular weight of X is
- 64.0
  - 32.0
  - 4.0
  - 8.0.
61. At STP which of the following real gases is likely to have the smallest molar volume (in m<sup>3</sup>)?
- oxygen
  - nitrogen
  - hydrogen
  - ammonia
62. The average velocity of an ideal gas molecules at 27°C is 0.3 m/sec. The average velocity at 927°C will be
- 0.6 m/sec
  - 0.3 m/sec
  - 0.9 m/sec
  - 3.0 m/sec
63. The ratio between the root mean square velocity of H<sub>2</sub> at 50 K and that of O<sub>2</sub> at 800 K is
- 1/4
  - 1
  - 2
  - 4
64. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends, the white ammonium chloride ring first formed will be
- at the centre of the tube
  - near the hydrogen chloride bottle
  - near the ammonia bottle
  - throughout the length of the tube.
65. Three identical flasks contain three different gases at standard temperature and pressure. Flask (P)
- contains CH<sub>4</sub>, flask (Q) contains CO<sub>2</sub>, flask (R) contains N<sub>2</sub>. Which flask contains the largest number of molecules?
- Flask (Q)
  - Flask (R)
  - Flask (P)
  - All three flasks have the same number of molecules
66. Equal masses of methane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is
- 1/2
  - 8/9
  - 1/9
  - 16/17
67. A flask filled with CCl<sub>4</sub> vapour was weighed at a temperature and pressure. The flask was then filled with oxygen at the same temperature and pressure. The mass of CCl<sub>4</sub> vapours would be about
- Five times as heavy as oxygen
  - Twice as heavy as oxygen
  - The same as that of the oxygen
  - One-fifth as heavy as oxygen
68. The ratio of root mean square velocity to average velocity of a gas molecule at a particular temperature is
- 1 : 1.086
  - 2 : 1.086
  - 1.086 : 1
  - 1.086 : 2
69. Equal weights of methane and oxygen are mixed in an empty container at 25°C. the fraction of the total pressure exerted by oxygen is
- 1/2
  - 2/3
  - $1/3 \times 273/298$
  - 1/3
70. A solution has a 1 : 4 mole ratio of pentane to hexane. The vapour pressures of the pure hydrocarbons at 20°C are 400 mm Hg for pentane and 120 mm Hg for hexane. The mole fraction of pentane in the vapour phase would be
- 0.200
  - 0.549
  - 0.786
  - 0.478
71. A general form of equation of state for gases is PV = RT [A + B/V + C/V<sup>2</sup> + ...], where V is the molar volume of the gas and A, B, C .... are constants for the gas. The values of A and B, if the gas obeys van der Waal's equation, are respectively
- $1, \frac{a}{27b}$
  - $1, b - \frac{a}{RT}$
  - $\frac{a}{RT}, b$
  - $\frac{2a}{RT}, b$

- 72.** Equation for Boyle's law is
- $\frac{d^2P}{P} = -\frac{dV}{dT}$
  - $\frac{d^2P}{P} = +\frac{d^2V}{dT}$
  - $\frac{dP}{P} = -\frac{dV}{V}$
  - $\frac{dP}{P} = +\frac{dV}{V}$
- 73.** If  $v_{rms}$  is  $30 \text{ R}^{1/2}$  at  $27^\circ\text{C}$ , then the molar mass of the gas in kilogram is
- 0.001
  - 0.1
  - 1.0
  - 2
- 74.** The density of a gas is  $1.964 \text{ g dm}^{-3}$  at  $273 \text{ K}$  and  $76 \text{ cm Hg}$ . The gas is
- $\text{CH}_4$
  - $\text{C}_2\text{H}_6$
  - $\text{CO}_2$
  - $\text{Xe}$
- 75.** The rate of effusion of two gases 'a' and 'b' under identical conditions of temperature and pressure are in the ratio of  $2 : 1$ . What is the ratio of rms velocity of their molecules if  $T_a$  and  $T_b$  are in the ratio of  $2 : 1$ ?
- $\sqrt{2} : 1$
  - $2 : 1$
  - $1 : \sqrt{2}$
  - $2\sqrt{2} : 1$
- 76.** Two gas bulbs A and B are connected by a tube having a stopcock. Bulb A has a volume of  $100 \text{ ml}$  and contains hydrogen. After opening the gas from A to the evacuated bulb B the pressure falls down by  $40 \%$ . The volume (ml) of B must be
- 75
  - 150
  - 125
  - 200
- 77.** A gas has double the average velocity of  $\text{SO}_2$  gas at any temperature. The gas may be
- $\text{CO}_2$
  - $\text{C}_2\text{H}_4$
  - $\text{CH}_4$
  - $\text{O}_2$
- 78.** If increases in temperature and volume of an ideal gas is two times, then the initial pressure P changes to
- $4P$
  - $2P$
  - $P$
  - $3P$
- 79.** Which of the following statement(s) regarding critical constants of van der Waal's gases is/are incorrect?
- Critical temperature of a gas is
  - The larger the  $T_c/P_c$  value of a gas, the larger would be the excluded volume.
  - At the critical point,  $(dp/dv) = 0$
- I and II
  - II and III
  - I and III
  - I only
- 80.**  $6.4 \text{ g SO}_2$  at  $0^\circ\text{C}$  and  $0.99 \text{ atm}$  pressure occupies a volume of  $2.241 \text{ L}$ . Predict which of the following is correct?
- the gas is ideal
  - the gas is real with intermolecular attraction
  - the gas is real without intermolecular repulsion
  - the gas is real with intermolecular repulsion greater than intermolecular attraction.
- 81.** An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If  $T_i$  is the initial temperature and  $T_f$  is the final temperature, which of the following statements is correct?
- $(T_f)\text{irrev} > (T_f)\text{rev}$
  - $T_f > T_i$  for reversible process but  $T_f = T_i$  for irreversible process
  - $(T_f)\text{irrev} = (T_f)\text{rev}$
  - $T_f = T_i$  for both reversible and irreversible processes
- 82.** A gaseous mixture of  $\text{NH}_3$  gas and  $\text{H}_2\text{S}$  gas contains  $20 \text{ mol}\%$  of  $\text{NH}_3$ . The vapour density of the mixture of
- 11.32
  - 25.2
  - 15.3
  - 18.6
- 83.** Dominance of strong repulsive forces among the molecules of the gas ( $Z$  = compressibility factor)
- depends on  $Z$  and indicated by  $Z = 1$
  - depends on  $Z$  and indicated by  $Z > 1$
  - depends on  $Z$  and indicated by  $Z > 1$
  - is independent of  $Z$ .
- 84.**  $X \text{ ml}$  of  $\text{H}_2$  effuse out through a hole in a container in  $5$  seconds. The time taken for the effusion of the same volume for the gas specified below under identical conditions is
- 25 sec; CO
  - 55 sec;  $\text{CO}_2$
  - 10 sec;  $\text{H}_2$
  - 20 sec;  $\text{O}_2$
- 85.** A monoatomic gas 'X' and a diatomic gas 'Y', both initially at the same temperature and pressure are compressed adiabatically from a volume  $V$  to  $V/2$ . The gas which has higher temperature is
- Y
  - X
  - Both have same temperature
  - Can not be said
- 86.** Equal masses of methane and oxygen are mixed in an empty container at  $25^\circ\text{C}$ . The fraction of the total pressure exerted by oxygen is

## 2.34 ■ Gaseous and Liquid States

- a.  $1/3 \times 273/298$       b.  $1/3$   
 c.  $1/2$       d.  $2/3$
87. A 4 : 1 mixture of helium and methane is contained in a vessel at 10 bar pressure. Due to a hole in the vessel, the gas mixture leaks out. The composition of mixture effusing out initially is  
 a. 1 : 1      b. 2 : 1  
 c. 4 : 1      d. 8 : 1
88. A large cylinder of helium filled at 2000 mm of Hg had a small orifice through which helium escaped into evacuated space at the rate of 6.4 moles/hour. How long would it take for 10 mole of CO to leak through a similar orifice if the CO were confined at the same pressure?  
 a. 6.5 hour      b. 8.4 hour  
 c. 4.2 hour      d. 12.4 hour
89. If the ratio of masses of  $\text{SO}_3$  and  $\text{O}_2$  gases confined in a vessel is 1 : 1, then the ratio of their partial pressures would be  
 a. 1 : 1      b. 1 : 2  
 c. 2 : 1      d. 2 : 5
90. What volume of oxygen gas ( $\text{O}_2$ ) measured at 0°C and 1 atm, is needed to burn completely one litre of propane gas ( $\text{C}_3\text{H}_8$ ) measured under the same conditions?  
 a. 5 L      b. 10 L  
 c. 7 L      d. 6 L
91. If the critical temperature of the gas be  
 $T_c = \frac{8a}{27Rb}$ .  
 and  $T_B$  is the Boyle's temperature, then which of the following is the correct relation between  $T_c$  and  $T_B$ ?  
 a.  $T_c = \frac{4}{27} T_B$       b.  $T_c = \frac{27}{6} T_B$   
 c.  $T_c = \frac{8}{27} T_B$       d.  $T_c = \frac{27}{8} T_B$
92. If a gas expands at constant temperature, it indicates that:  
 a. Kinetic energy of molecules remains the same  
 b. Number of the molecules of gas increases  
 c. Kinetic energy of molecules decreases  
 d. Pressure of the gas increases
93. In order to increase the volume of a gas by 10%, the pressure of the gas should be  
 a. Decreased by 10%  
 b. Decreased by 1%
94. Critical temperature and critical pressure value of four gases are given
- | Gas | Critical temp<br>(K) | Critical press.<br>(atm) |
|-----|----------------------|--------------------------|
| A   | 5.1                  | 2.2                      |
| B   | 33                   | 13                       |
| C   | 126                  | 34                       |
| D   | 135                  | 40                       |
- Which of the following gas/gases cannot be liquefied at a temperature 100 K and pressure 50 atm?  
 a. A and B      b. C and D  
 c. A and D      d. A, B and D
95. Which of the following is the correct increasing order of compressibility of the gases  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{O}_2$ ,  $\text{NH}_3$ ?  
 a.  $\text{O}_2 < \text{NH}_3 < \text{CO} < \text{CO}_2$   
 b.  $\text{NH}_3 < \text{O}_2 < \text{CO} < \text{CO}_2$   
 c.  $\text{CO}_2 < \text{CO} < \text{NH}_3 < \text{O}_2$   
 d.  $\text{NH}_3 < \text{O}_2 < \text{CO}_2 < \text{CO}$
96. Let the most probable velocity of hydrogen molecules at a temperature  $t^\circ\text{C}$  is  $V_0$ . Suppose all the molecules dissociate into atoms when temperature is raised to  $(2t + 273)^\circ\text{C}$  then the new r.m.s. velocity is  
 a.  $2\sqrt{3} V_0$       b.  $\sqrt{6} V_0$   
 c.  $\sqrt{(2/3)} V_0$       d.  $\sqrt{[3(2 + 273/t)]} V_0$

### Multiple Correct Answer Type Questions

97. The factor which measure the deviation from ideal behaviour of a gas are  
 a. collision frequency  
 b. collision diameter  
 c. compressibility factor  
 d. Van der Waal's constant 'a'
98. The correct statement(s) amongst the following is/are  
 a. A gas above its critical temperature can be liquefied by applying the minimum pressure  
 b. Deviation of real gases from ideal behaviour becomes more pronounced as pressure is increased and temperature is decreased.

c. At  $0^{\circ}\text{C}$ ,  $\text{H}_2$  and  $\text{He}$  show positive deviation throughout with increasing pressure indicating thereby that the Boyle's temperatures for these two gas are below  $0^{\circ}\text{C}$

d.  $\text{N}_2(\text{g})$  shows ideal behaviour for some range of pressure ( $0 - 100\text{ atm}$ ) at  $51.1^{\circ}\text{C}$  indicating that  $51.1^{\circ}\text{C}$  is the Boyle's temperature for  $\text{N}_2(\text{g})$ .

99. Which is/are not correct according to the kinetic theory of gases?

- a. the pressure exerted by a gas is proportional to mean square velocity of the molecules
- b. the pressure exerted by the gas is proportional to the root mean square velocity of the molecules
- c. the root mean square velocity is inversely proportional to the temperature
- d. the mean translational K.E. of the molecule is directly proportional to the absolute temperature.

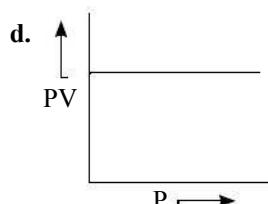
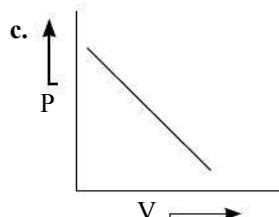
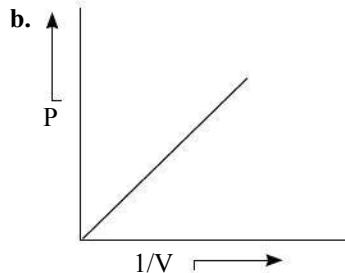
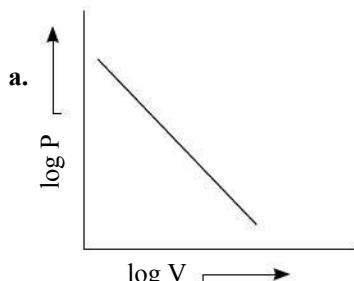
100. Which of the following statement(s) is/are true about the effect of an increase in temperature on the distribution molecular speeds in a gas?

- a. the most probable speed increases
- b. the fraction of the molecules with the most probable speed increases
- c. the distribution becomes broader
- d. the area under the distribution curve remains the same as the under the lower temperature

101. If a gas expands at constant temperature

- a. the pressure decreases
- b. the kinetic energy of the molecules remains the same
- c. the kinetic energy of the molecules decreases
- d. the number of molecules of the gas increase.

102. Which of the following graphs represents Boyle's law?



103. Which of the following gases fairly deviates from ideal behaviour?

- a.  $\text{H}_2$
- b.  $\text{NH}_3$
- c. He
- d.  $\text{SO}_2$

104. Which of the following statement is/are correct on the basis of Charle's law here?

- a. The pressure of an ideal gas can be zero.
- b. The volume of an ideal gas can never be zero.
- c. It is not possible to achieve absolute zero temperature.
- d. At zero pressure, all molecular motion ceases in a gas, and it does not exert any pressure on the walls of the container.

105. Which of the following is/are the characteristics of a real gas?

- a. It obeys the gas law at low temperature and high pressure
- b. The gas molecules attract each other
- c. It shows deviation from the ideal gas law
- d. The mass of gas molecule is negligible

## 2.36 ■ Gaseous and Liquid States

106. Which of the following statement is/are correct here?
- Gases cannot be directly condensed into solids without passing through liquid state
  - Gases and liquids have viscosity as common property
  - Gases and liquids have pressure as common property
  - Particles in all the three states have random translational motion.
107. At constant volume, for a fixed number of mole of a gas, the pressure of the gas increases with rise of temperature due to
- Increased rate of collisions amongst molecules
  - Decrease in mean free path
  - Increase in average molecular speed
  - Increase in molecular attraction
108. Which of the following masses of gas would occupy about  $3 \text{ dm}^3$  at  $25^\circ\text{C}$  and one atmosphere?
- 2.25 g of Neon
  - 8.0 g of  $\text{SO}_2$
  - 5.5 g of  $\text{CO}_2$
  - 4.0 g of  $\text{O}_2$
109. Which of the following equation(s) is/are incorrect on the basis of ideal gas equation?
- $\text{PV} = \frac{d}{m} \text{RT}$
  - $\text{PV} = d\text{RT}$
  - $\text{PV} = \frac{N}{N_0} \text{RT}$
  - $\text{PV} = Nk_B T$
- (Here  $N$  = number of molecules,  $N_0$  = Avogadro's number,  $k_B$  = Boltzmann constant)
110. A two litre flask containing 4 g of oxygen is heated from  $27^\circ\text{C}$  to  $327^\circ\text{C}$ . Which of the following statements are correct?
- The number of mole of the gas increases
  - The energy of the gaseous molecules increases
  - The pressure of the gas increases
  - The rate of collision increases
111. Which of the following is correct for critical temperature?
- At this temperature, the surface tension of the system is very high.
  - At this temperature, the gas and the liquid phases have different critical densities.
112. Which of the following statements is/are correct regarding marsh gas indicator
- It can be used at marshy places only
  - It measures the rate of radioactive disintegration of  $^{14}\text{C}$  in methane
  - It is used to detect the presence of excess of methane in coal mines
  - Its working is based upon Graham's law of diffusion
113. Four gas balloons P, R, Q and S of equal volumes containing,  $\text{H}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$  respectively were pricked with needle and immersed in a tank concentration  $\text{CO}_2$ . Which of them will shrink after some time?
- P
  - Q
  - R
  - S
114. At low pressures, the van der Waal's gas equation for 1 mole of a gas may be written as
- $\text{PV} = \text{RT} - \frac{a}{V}$
  - $\text{PV} = \text{RT}$
  - $\text{PV} = \text{RT} + Pb$
  - $\text{P} + \frac{a}{V^2} = \frac{\text{RT}}{V}$
115. A gas can be easily liquefied:
- Under reversible adiabatic expansion
  - At low pressure and above critical temperature
  - When its inversion temperature equals the Boyle's temperature
  - Under pressure when it is cooled below the critical temperature
116. Which statement is/are correct regarding van der Waal's constant 'a' and 'b'?
- 'b' is excluded or co-volume of the gas
  - 'a' is the measure of force of attraction in between the particles
  - Lower is the value of 'b', easier is the liquefaction of the gas
  - Higher is the value of 'a', easier is the liquefaction of the gas

117. If the volume of two gases X and Y are the same under identical conditions of temperature and pressure. Then they would differ in

- a. Rate of diffusion
- b. Kinetic energy
- c. Boiling point
- d. Number of molecules

118. The correct relation is

$$\begin{array}{ll} \text{a. } V_c = 3b & \text{b. } \frac{P_c V_c}{RT_c} = \frac{3}{8} \\ \text{c. } T_c = \frac{8a}{27 Rb} & \text{d. } P_c = \frac{a}{27 b^2} \end{array}$$

119. According to Maxwell-Boltzman distribution of speeds among gas molecules, what is true?

- a. The value of r.m.s. increases with rise in temperature
- b. Area under the curve gives the total number of molecules.
- c. The maxima in plot of  $\Delta N/N$  vs speeds pertains to average speed
- d. The plot of  $\Delta N/N$  vs speeds is straight line with slope  $> 0$

120. Which of the following statement about molecules of gaseous hydrogen and oxygen is/are correct here?

- a. At the same temperature, the hydrogen molecules will have the greater speed
- b. At the same temperature, the mean kinetic energies will be equal
- c. The mean molecular velocity increases with temperature in each case.
- d. The mean speed is directly proportional to the temperature in each case

121. Which of the following statement is/are correct?

- a. Helium escapes at a rate 2 times as fast as  $O_2$  does.
- b. Helium escapes at a rate 4 times as fast as  $SO_2$  does.
- c. Helium escapes at a rate 2.65 times as fast as CO does.
- d. Helium diffuses at a rate 8.65 times as much as CO does.

122. Van der Waal's constants for three different gases are given:

Gas	a	b
A	3.0	0.025
B	10.0	0.030
C	6.0	0.035

Which of these is correct?

- a. Most easily liquefiable gas is A
- b. Maximum critical temperature – B
- c. Maximum molecular volume – C
- d. Most ideal behaviour – A

123. The incorrect statement/s is/are

- a. Gases tend to become ideal at inversion temperature
- b. Gases tend to become ideal at Boyle's temperature over a wide range of pressure
- c. Gases deviate maximum from ideal behaviour when the temperature is very high and pressure is very low.
- d. Gases deviate minimum from the ideal behaviour when the temperature is very low and pressure is very high.

124. Consider the following equation:

$$PV_m = RT \left(1 + \frac{B}{V_m} + \frac{B}{V_m^2} + \dots\right)$$

Here which statement is/are correct about  $V_m$ ?

- a. It is independent of temperature
- b. It is equal to  $RT/P$  at Boyle's temperature
- c. It has the dimension of molar volume
- d. It is equal to  $P/RT$  at critical temperature

125. Which of the following matching is/are incorrect?

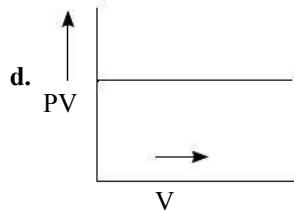
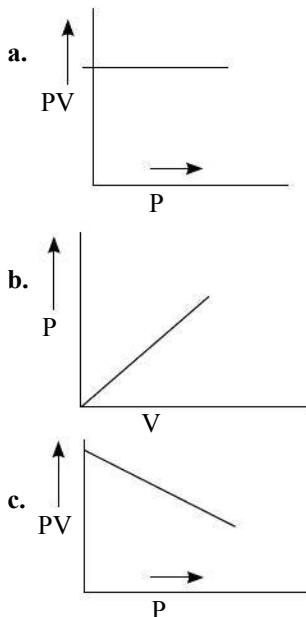
- a.  $a/Rb \dots T_c$
- b.  $(8 kT/\pi m)^{1/2} \dots u_{rms}$
- c.  $8aRT/27 \dots$  Boyle's temperature
- d.  $(3PV/M)^{1/2} \dots \alpha$

126. Indicate the correct statement for equal volumes of  $N_2(g)$  and  $CO_2(g)$  at  $25^\circ C$  and 1 atm.

- a. The rms speed remains constant for both  $N_2$  and  $CO_2$
- b. The average translational KE per molecule is the same for  $N_2$  and  $CO_2$

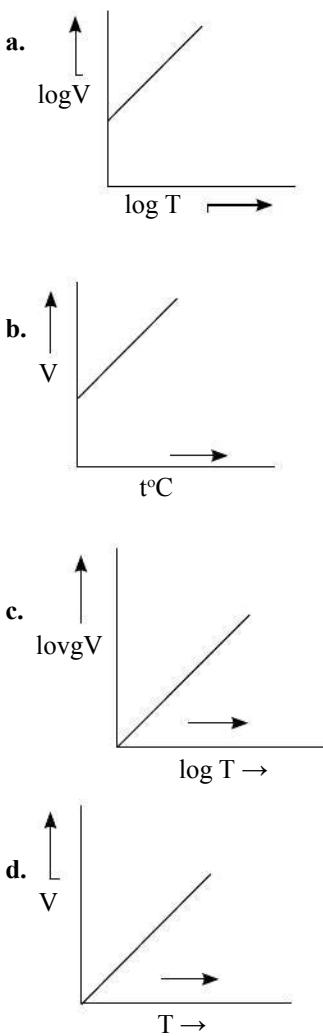
## 2.38 ■ Gaseous and Liquid States

- c. The total translational KE of both  $N_2$  and  $CO_2$  is the same
- d. The density of  $N_2$  is more than that of  $CO_2$
127. Which of the following statement is/are correct?
- At a temperature below  $T_c$ , the molecules are close enough for the attractive forces to act, the condensation occurs.
  - The kinetic energy of the gas molecules is higher above  $T_c$ , and the attraction between temperature decreases.
  - No condensation takes place above  $T_c$ .
  - It is not possible to compress a gas at a temperature below  $T_c$ .
128. When an ideal gas is allowed to expand into another evacuated vessel through a tiny hole, then
- The temperature of the gas remains constant
  - The temperature of the gas is decreased
  - There is no intermolecular force of attraction between an ideal gas
  - Energy is absorbed from the surroundings
129. Which of these quantities are same for all ideal gases at any particular temperature?
- The number of molecules in 1 gm
  - The kinetic energy of 1 mole
  - The kinetic energy of 1 gm
  - The number of molecules in 1 mole
130. Which of the following graphs does not represent Boyle's law



131. If two vessels of equal volumes have  $H_2$  and  $He$  at 1 and 2 atm pressure respectively at the same temperature. Then which relation is/are correct?
- $u_{rms} H_2 = u_{rms} He$
  - $r_{H_2} = r_{He}/\sqrt{2}$
  - $u_{rms} H_2 = \sqrt{2} u_{rms} He$
  - $r_{H_2} = \sqrt{8} \times r_{He}$
132. The correct statement about van der Waal's constant 'b' is/are
- It depends on intermolecular force
  - Its value depends on molecular size
  - It is exclude volume
  - Its unit is mole per litre.
133. Which of the following statement is/are correct here?
- Larger is the excluded volume of gas, less will be its critical volume
  - Larger is the value of  $T_c/P_c$  for a gas larger would be its excluded volume
  - The excluded volume for  $He$  is more than  $H_2$ .
  - The slope for an isochore obtained for a gas showing  $P(V - b) = RT$  is  $[R/(V - b)]$
134. 4.4 g  $CO_2$  gas and 2.24 l of  $H_2$  gas are taken in a one litre container at 300 K. The total pressure of the gas in container will be
- 14.856 atm
  - 4378.15 mm of Hg
  - 4.926 atm
  - 3743.76 mm of Hg
135. Which is/are correct for molecular speed of gases?
- $u_{rms} > u_{av}$
  - $u_{mp} = \sqrt{(8RT/\pi M)}$
  - $u_{rms} = \sqrt{(3PV/M)}$
  - $u_{mp} > u_{av}$

136. Which of the following graph correctly represents Charle's law?



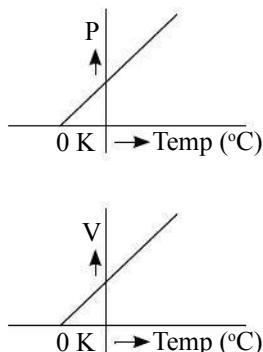
137. Regarding  $\text{H}_2$  gas, the correct statement(s) is/are
- The critical temperature of  $\text{H}_2$  gas is very high
  - The value of van der Waal's constant 'a' is very low for  $\text{H}_2$
  - For  $\text{H}_2$  gas,  $Z > 1$  at  $0^{\circ}\text{C}$
  - When  $\text{H}_2$  gas expands at above inversion temperature, then it shows heating effect

138. Which of the following statements are correct?
- He escapes at a rate of 2.65 times as fast as  $\text{CO}$  does
  - He diffuses at a rate of 4.65 times as much as  $\text{CO}$  does

- c. He escapes at a rate of 4 times as fast as  $\text{SO}_2$  does  
d. He escapes at a rate of 8 times as  $\text{CO}_2$  does
139. A 50 ml sample of a hydrogen-oxygen mixture was placed in a gas burette at  $18^{\circ}\text{C}$  and confined at 1 atm. A spark was passed through the sample so that the formation of water could go to completion. The resulting pure gas had a volume of 10 ml at atmospheric pressure. The initial mole fraction of hydrogen in the mixture would be

- a. 0.534      b. 0.734  
c. 0.634      d. 1.534

140. What conclusion would you draw from the following graphs?



- a. As the temperature is lowered, the volume as well as the pressure increases  
b. As the temperature is lowered, the volume as well as the pressure decreases  
c. A point is reached where, theoretically, the volume as well as the pressure become zero.  
d. As the temperature is lowered, the volume becomes zero and the pressure becomes infinity.

### Linked-Comprehension Type Questions

#### Comprehension 1

**Graham's Law of Diffusion:** The phenomenon of spontaneous intermixing of gases against the law of gravitation is known as diffusion. If diffusion occurs through small orifice of the container then it is known as effusion.

The rate of diffusion is expressed as

$$\text{Rate of diffusion} = \frac{\text{Volume of gas diffused}}{\text{Time}}$$

$$= \frac{\text{Moles of gas diffused}}{\text{Time}}$$

## 2.40 ■ Gaseous and Liquid States

$$= \frac{\text{Distance travelled by gas}}{\text{Time}} = \frac{1}{\sqrt{M}}$$

Here M = molar mass of gas.

141. 100 ml of O<sub>2</sub> gas diffuses in 10 seconds. 100 ml of gas 'X' diffuses in 't' seconds. Gas 'X' and time 't' can be respectively
- He, 4 seconds
  - H<sub>2</sub>, 2.5 seconds
  - SO<sub>2</sub>, 14 seconds
  - CO, 12 seconds
142. 1 mole of gas H<sub>2</sub> and 4 moles of gas O<sub>2</sub> is taken inside the vessel, which effuse through the small orifice of the vessel having same area of cross section and at the same temperature, then which of the correct percentage of effused volume of gas H<sub>2</sub> and O<sub>2</sub> initially respectively? (Assume that the gas H<sub>2</sub> does not react with O<sub>2</sub> gas)
- 25% and 75%
  - 20% and 80%
  - 50% and 50%
  - 65% and 34%
143. He and Ar are monoatomic gases and their atomic weights are 4 and 40 respectively. Under similar conditions He will diffuse through semi permeable membrane
- 13 times as fast as Ar
  - 3.16 times as fast as Ar
  - 16 times as fast as Ar
  - 5.62 times as fast as Ar

### Comprehension 2

The van der Waal's equation of state for one of a mole real gas is written as

$$[P + \frac{a}{V^2}] (V - b) = RT$$

The virial equation for one mole of a real gas is given as follows:

$$PV = RT [1 + \frac{X}{V} + \frac{Y}{V^2} + \frac{Z}{V^3} + \dots \text{to higher power of 'n'}]$$

Here X, Y and Z are constants which are known as second, third and fourth virial coefficient respectively.

The temperature at which real gas obeys ideal gas equation i.e., (PV = nRT) is known as Boyle's temperature.

144. The third virial coefficient of a He gas is  $4 \times 10^{-2}$  (litre/mole)<sup>2</sup> then what will be volume of 2 mole He gas at NTP?

- 45.2 lit
- 11.3 lit
- 22.6 lit
- 4.52 lit

145. If the critical temperature of the gas be

$$T_c = \frac{8a}{27 Rb}$$

and T<sub>B</sub> is the Boyle's temperature, then the correct relation between T<sub>c</sub> and T<sub>B</sub> is

- $T_c = \frac{4}{27} T_B$
- $T_c = \frac{27}{6} T_B$
- $T_c = \frac{8}{27} T_B$
- $T_c = \frac{27}{8} T_B$

146. Which of the following is the incorrect statement about the Boyle's temperature (T<sub>B</sub>)?

- The value of T<sub>B</sub> is equal to a/Rb
- Temperature at which second virial coefficient becomes zero
- Temperature at which first virial coefficient becomes zero
- Both a. and b.

### Comprehension 3

The density of the vapour of a substance at one atmospheric pressure and 500 K temperature is 0.36 kg m<sup>-3</sup>. The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under same conditions of temperature and Pressure.

147. The molecular weight of the vapour is?

- 36
- 18
- 27
- 9

148. The value of compressibility factor (Z) for this vapour is?

- 1.11
- 2.44
- 1.22
- 2.22

149. If the vapour shows ideal gas behaviour at 1000 K than its average transitional kinetic energy will be?

- $1.035 \times 10^{-10}$  J
- $2.07 \times 10^{-30}$  J
- $4.41 \times 10^{-20}$  J
- $2.07 \times 10^{-20}$  J

### Comprehension 4

As in reality no gas shows behaviour of ideal gas and such gases are known as real gases. In order to modify ideal gas equation for such gases van der Waal introduced an equation as follows:

$$(P + a \frac{n^2}{V^2})(V - nb) = nRT$$

Here constant 'a' is an indirect measurement of magnitude of attractive force present between the molecules of the gas. Its higher value shows ease of liquefaction.

The constant 'b' is known as covolume or excluded volume. It is four times of the actual volume occupied by a molecule.

- 150.** Gases X, Y, Z and P have the Van der Waal's constants 'a' and 'b' (in CGS) as follows:

	X	Y	Z	P
a	6	620	0.05	
b	0.025	0.15	0.1	0.02

The gas with the highest critical temperature is:

- a. P
- b. X
- c. Y
- d. Z

- 151.** At high pressure, Van der Waal's equation becomes:

- a.  $PV = RT + a/V$
- b.  $PV = RT$
- c.  $PV = RT + Pb$
- d.  $PV = RT - a/V$ .

- 152.** Which of the following statement is incorrect here?

- a. More the value of excluded volume of a gas more will be its critical volume
- b. The excluded volume of hydrogen is less than that of helium
- c. Higher the value of  $T_c/P_c$  for a gas more is the value of its excluded volume
- d. Ammonia is more easily liquefied than hydrogen

- 153.** Find Boyle's temperature range in case of  $\text{CO}_2$  if for it the values of 'a' and 'b' are 3.592 atm  $\text{lit}^2/\text{mol}^2$  and 0.0427  $\text{lit}/\text{mole}$  respectively

- a. 752°C
- b. 650°C
- c. 562°C
- d. 572°C

- 154.** The gas equation for a real gas is:

$$P(V - b) = RT$$

Here, the parameter 'b' is Van der Waal's constant. The graph of pressure against temperature (isochore) will give straight line of slope:

- a. Negative
- b. Zero
- c.  $R/(V - b)$
- d.  $R/P$

## Comprehension 5

The van der Waals equation is one of the equation many equation of state suggested in order to account for the behaviour of real gases. There are two other simple equations of state which involve just two arbitrary constants. The first of these, equation given as follow

$$(P + a \frac{n^2}{T V^2})(V - nb) = nRT$$

Here a and b are known as Berthelot's constants and are characteristics of the gas.

The second equation, Dieterici, is given as  
 $\{pexp(na/VRT}\} (V - nb) = nRT$

All these three equation of state can be expressed approximately in one common form, known as the virial equation of state it can be given as

$$Z = \frac{pVm}{RT} = 1 + B \frac{1}{Vm} + C \frac{1}{V^2 m} + D \frac{1}{V^3 m} + \dots$$

here B,C, ....are temperature dependent constants known as second, third, etc., virial coefficients.

- 155.** The van der Waals and the Dieterici equation can give the same value of P at

- a. High Density
- b. Low Density
- c. At no temperature
- d. At Entity

- 156.** When a graph is plotted between  $V_m \{pVm/RT - 1\}$  versus  $1/V_m$  is extra plotted to  $1/V_m = 0$  we get the value of

- a. A
- b. B
- c. C
- d. Any of these

- 157.** The numerical value of virial coefficients .....very sharply with higher powers of volume

- a. Decrease
- b. Increase
- c. Increase or Decrease
- d. First increase than decrease

## Assertion-Reason Type Questions

In the following question, two statements (Assertion) A and Reason (R) are given. Mark

- a. if A and R both are correct and R is the correct explanation of A;
- b. if A and R both are correct but R is not the correct explanation of A;
- c. A is true but R is false;
- d. A is false but R is true,
- e. A and R both are false.

## 2.42 ■ Gaseous and Liquid States

- 158.** (A): The viscosity of an ideal gas is independent of pressure at constant temperature.  
 (R): As the pressure is increased, the effect of the increase in number density of molecules is compensated by a proportionate decrease in the mean free path.
- 159.** (A): Considering van der Waal's equation of state for a real gas ( $P + n^2a/V^2$ )  
 $(V - nb) = nRT$ ; The constant 'a' for O<sub>2</sub> is less than that for H<sub>2</sub>O (g).  
 (R): The molar mass of O<sub>2</sub> is almost twice that of H<sub>2</sub>O
- 160.** (A): In the Joule-Thomson expansion of hydrogen and helium, the temperature of the gases increases.  
 (R): These gases have very high inversion temperature.
- 161.** (A): The heat capacities of all the diatomic molecules attain a limiting value at higher temperatures.  
 (R): At room temperature, the translational and rotational degrees of freedom contribute to the heat capacities of gases, while the vibrational degree of freedom becomes active only at higher temperatures.
- 162.** (A): All molecules of an ideal gas move with the same speed.  
 (R): There is no attraction between the molecules in an ideal gas.
- 163.** (A): Considering the van der Waal's equation of state  
 $(P + a/V^2) + (V - b) = RT$   
 for ammonia (NH<sub>3</sub>) and nitrogen (N<sub>2</sub>), the value of a for NH<sub>3</sub> is larger than that of N<sub>2</sub>.  
 (R): Ammonia has a lower molecular weight than nitrogen.
- 164.** (A): The hydrogen gas warms up during the Joule-Thomson expansion.  
 (R): The temperature at which the Joule Thomson coefficient becomes negative is called Joule-Thomson inversion temperature
- 165.** (A): The gases He and CO<sub>2</sub> are very different in their behaviour at any temperature and pressure, but their compressibility factors are nearly the same.  
 (R): The 'Law of corresponding states' states that the compressibility factor of any gas can be written as a universal function of the reduced variables.
- 166.** (A): In Van der Waal's equation ( $P + a/V^2$ ) ( $V - b$ ) = RT pressure correction ( $a/V^2$ ), is due to force of attraction between molecules.  
 (R): Due to force of attraction, volume of molecules cannot be neglected.
- 167.** (A): A lighter gas diffuses more rapidly than a heavier gas.  
 (R): At a given temperature, the rate of diffusion of a gas is inversely proportional to the square root of its density.
- 168.** (A): When temperature of an ideal gas increases from 27°C to 127°C at constant P, volume increases by 100 L.  
 (R):  $V \propto T$  at constant P.
- 169.** (A): Van der Waal's constant 'a' is a measure of force of attraction between molecules.  
 (R): This constant is the volume correction.
- 170.** (A):  $C_p - C_v = R$  for an ideal gas  
 (R): R is the work done when temperature of one mol of an ideal gas is increased by 1°.
- 171.** (A): Van der Waal's 'b' is expressed in the unit of atm L<sub>2</sub> mol<sup>-2</sup>.  
 (R): 'b' is pressure correction due to force of attraction.
- 172.** (A):  $C_p - C_v = R$  for an ideal gas  
 (R):  $(\partial E/\partial V)_T = 0$  for an ideal gas
- 173.** (A): The Joule-Thomson coefficient for an ideal gas is zero.  
 (R): There are no intermolecular attractive forces in an ideal gas.
- 174.** (A): H<sub>2</sub> and He show some ideal gas behaviour.  
 (R): All real gases deviate from ideal gas behaviour at low temperature and high pressure
- 175.** (A): An ideal gas cannot be liquefied even by attaining 0.003 K with the help of adiabatic demagnetization.  
 (R): The Van der Waal's constant 'a' is negligible for an ideal gas and molecules are assumed as point mass.
- 176.** (A): 8 grams of methane occupies 11.207 litres of volume at 273 K and 1 atm pressure.  
 (R): one mole of any gas at STP occupies 22.414 litres of volume.

**177. (A):** The heat capacities of all the diatomic molecules attain a limiting value at higher temperature.

**(R):** At room temperature, the translational and rotational degrees of freedom become active only at higher temperature.

**178. (A):** The triple point of a pure substance having three phases in equilibrium has zero degree of freedom.

**(R):** None of the variables like temperature and pressure can be changed without change in the number of phases.

**179. (A):** Whatever be the temperature, liquid  $\text{CO}_2$  does not exist at normal atmospheric pressure.

**(R):** The triple point of  $\text{CO}_2$  lies above 1.0 atm.

**180. (A):** A value of Van der Waal's constant 'a' is larger for  $\text{NH}_3$  than  $\text{PH}_3$ .

**(R):** Hydrogen bonding is present in  $\text{NH}_3$ .

**181. (A):** Absolute zero is the lowest possible temperature.

**(R):** A lower temperature would correspond to negative value of volume of gas which is physically meaningless.

**182. (A):**  $\text{H}_2$  when allowed to expand at room temperature, it causes heating effect.

**(R):**  $\text{H}_2$  has inversion temperature much below room temperature.

### Matrix-Match Type Questions

	p	q	r	s
(A)	O	O	O	O
(B)	O	O	O	O
(C)	O	O	O	O
(D)	O	O	O	O

**183. Match the following:**

**Column I**                    **Column II**

- |                               |                          |
|-------------------------------|--------------------------|
| A. Rate of effusion/diffusion | (p) Absolute temperature |
| B. Kinetic energy             | (q) Mole fraction        |
| C. Partial pressure of a gas  | (r) Density              |
| D. Liquification of a gas     | (s) Critical temperature |
|                               | (t) Value of 'a'         |

**184. Match the following**

<b>Column I</b>	<b>Column II</b>
A. Critical temperature	(p) $\text{Litre mol}^{-1}$
B. Co-volume (b)	(q) $8a/27 Rb$
C. Molar volume of a gas at NTP (22.4)	(r) $\text{Lit}^2 \text{ atm mol}^{-2}$
D. Van der Waal's constant (a)	(s) $M^4 \text{ newton mol}^{-2}$

**185. Match the following:**

<b>Column I</b>	<b>Column II</b>
A. Boyle's law	(p) $\frac{d_1 t_2}{d_2 t_1} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$
B. Graham diffusion law	(q) $P_1 V_1 = P_2 V_2$
C. Avogadro law	(r) $V_1/n_1 = V_2/n_2$
D. Kinetic equation	(s) $(\delta P/\delta V)_T = -K/V^2$
	(t) $PV = 1/3 mn u_{\text{rms}}^2$

**186. Match the following:**

<b>Column I (Gases)</b>	<b>Column II (Van der Waal's constant 'a')</b>
A. He	(p) 2.25
B. $\text{CH}_4$	(q) 3.59
C. $\text{SO}_2$	(r) 6.71
D. $\text{CO}_2$	(s) 0.034

**187. Match the following:**

**Column I**                    **Column II**

- |                                      |                      |
|--------------------------------------|----------------------|
| A. $P \propto 1/V$ at constant T     | (p) Graham's law     |
| B. $P \propto T$ at constant V       | (q) Gay Lussac's law |
| C. $V \propto T$ at constant P       | (r) Charle's law     |
| D. $V \propto n$ at constant T and P | (s) Boyle's law      |

## 2.44 ■ Gaseous and Liquid States

188. Match the following:

Column I	Column II
A. Critical temperature	(p) $a/R_b$
B. Boyle temperature	(q) $2a/R_b$
C. Inversion temperature	(r) $T/T_c$
D. Reduced temperature	(s) $8a/27 R_b$

189. Match the following:

Column I	Column II
A. RMS speed	(p) $3/2 RT$
B. Average speed	(q) $\sqrt{8 KT/nm}$
C. Mole fraction	(r) $\sqrt{3KT/m}$
D. Kinetic energy of more atoms of gas	(s) $n/\sum n$

190. Match the following:

Column I	Column II
A. Dalton's law	(p) $v_1/v_2 = \sqrt{(M_2/M_1)}$ (at constant temp. & pressure)
B. Dulong and Petit's Law	(q) At. wt x Specific heat $\approx 6.4$
C. Graham's Law	(r) $P_{\text{gas}} = x_{\text{gas}} \times K_H$
D. Henry's law	(s) $P_A = \text{mole fraction} \times \text{Total pressure}$

191. Match the following:

Column I	Column II
A. Gas constant (R)	(p) mol dm <sup>-3</sup>
B. Ionic product of water (Kw)	(q) mol <sup>2</sup> dm <sup>-6</sup>
C. Van der Waal's constant (A)	(r) dm <sup>3</sup> atm K <sup>-1</sup> mol <sup>-1</sup>
D. Equilibrium constant of HA <sub>c</sub> (k)	(s) dm <sup>6</sup> atm mol <sup>-2</sup>

192. Match the following:

Column I	Column II
A. $(2RT/M)^{1/2}$	(p) torr
B. work done degree <sup>-1</sup> mol <sup>-1</sup>	(q) gram molar volume
C.-22.4 litre at S.T.P	(r) universal gas constant
D. unit of low pressure	(s) most probable velocity

193. Match the following:

Column I	Column II
A. density of ideal gas	(p) effusion
B. escape of gas from punctured tube	(q) $\sqrt{8RT/\pi M}$
C. average speed	(r) $\sqrt{3RT/M}$
D. R.M.S velocity	(s) $ML^2T^{-1}\theta$
	(t) $PM/RT$

194. Match the following:

Column I (Gases under specified condition)	Column II (Properties)
A. Hydrogen gas ( $P = 200$ atm, $T = 273$ K)	(p) Compressibility factor $\neq 1$
B. Hydrogen gas ( $P \sim 0$ , $T = 273$ K)	(q) Attractive forces are dominant
C. $CO_2$ ( $P = 1$ atm, $T = 273$ K)	(r) $PV = nRT$
D. Real gas with very large molar volume	(s) $P(V - nb) = nRT$

[IIT 2007]

### The IIT-JEE Corner

195. The compressibility factor for an ideal gas is

- a. 1.5
- b. 1.0
- c. 2.0
- d.  $\infty$

[IIT 1997]

196. The critical temperature of water is higher than that of  $O_2$  because the  $H_2O$  molecule has

- a. fewer electrons than  $O_2$
- b. two covalent bonds
- c. V-shape
- d. dipole moment

[IIT 1997]

197. The following statement (s) is (are) correct

- (1) A plot of  $\log K_p$  versus  $1/T$  is linear
- (2) A plot of  $\log (X)$  versus time is linear for a first order reaction  $X \rightarrow P$
- (3) A plot of  $\log P$  versus  $1/T$  is linear at constant volume
- (4) A plot of  $P$  versus  $1/V$  is linear at constant temperature.

a. 1, 2

c. 2, 3

b. 2, 4

d. 1, 4

[IIT 1999]

198. At  $100^{\circ}\text{C}$  and 1 atm. if the density of liquid water is  $1.0 \text{ g cm}^{-3}$  and that of water vapour is  $0.0006 \text{ g cm}^{-3}$ , then the volume occupied by water molecules in 1 litre of steam at that temperature

a.  $6 \text{ cm}^3$ b.  $60 \text{ cm}^3$ c.  $0.6 \text{ cm}^3$ d.  $0.06 \text{ cm}^3$ 

[IIT 2000]

199. The compressibility factor of a gas is less than unity at STP. Therefore

a.  $V_m > 22.4 \text{ litres}$ b.  $V_m < 22.4 \text{ litres}$ c.  $V_m = 22.4 \text{ litres}$ d.  $V_m = 44.8 \text{ litres}$ 

[IIT 2000]

200. The r.m.s. velocity of hydrogen is  $\sqrt{7}$  times the r.m.s. velocity of nitrogen. If T is the temperature of the gas

a.  $T(\text{H}_2) = T(\text{N}_2)$ b.  $T(\text{H}_2) > T(\text{N}_2)$ c.  $T(\text{H}_2) < T(\text{N}_2)$ d.  $T(\text{H}_2) = \sqrt{7} T(\text{N}_2)$ 

[IIT 2000]

201. The root mean square velocity of a ideal gas at constant pressure varies with density d as

a.  $d^2$ 

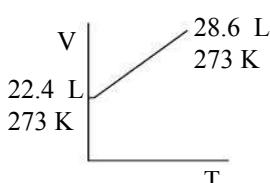
b. d

c.  $\sqrt{d}$ d.  $1/\sqrt{d}$ 

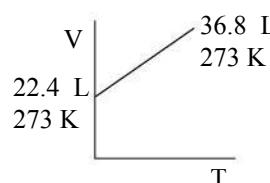
[IIT 2001]

202. Which of the following volume (V)-temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure?

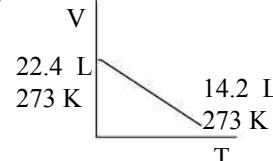
a.



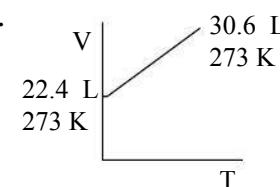
b.



c.



d.



203. Positive deviation from ideal behaviour takes place because of

a. molecular interaction between atoms and  $\frac{PV}{nRT} > 1$ b. molecular interaction between atoms and  $\frac{PV}{nRT} < 1$ c. finite size of atoms and  $\frac{PV}{nRT} > 1$ d. finite size of atoms and  $\frac{PV}{nRT} < 1$ 

[IIT 2003]

204. The root mean square velocity of one mole of a monoatomic gas having molar mass M is Urms. The relation between the average kinetic energy (E) of the gas and Urms is

a.  $Urms = \sqrt{(3E/2M)}$ b.  $Urms = \sqrt{(2E/3M)}$ c.  $Urms = \sqrt{(2E/M)}$ d.  $Urms = \sqrt{(E/3M)}$ 

[IIT 2004]

205. The ratio of rate of diffusion of helium with respect to methane under similar conditions of constant temperature and pressure

a. 2

b. 0.5

c. 16

d. 4

[IIT 2005]

206. A monoatomic ideal gas undergoes a process in which the ratio of P to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas?

a.  $4R/2$ b.  $3R/2$ c.  $5R/2$ 

d. 0

[IIT 2006]

207. A gas described by van der Waal's equation

a. Behaves similar to an ideal gas in the limit of large molar volumes

## **2.46 ■ Gaseous and Liquid States**

- b. Behaves similar to an ideal gas in the limit of large pressures
  - c. Is characterized by van der Waal's coefficients that are dependent on the identity of the gas but are independent of the temperature
  - d. Has the pressure that is lower than the pressure exerted by the same gas behaving ideally

[HT 2008]

208. The terms that corrects for the attractive forces present in a real gas in the van der Waals equations

  - a. nb
  - b.  $\frac{an^2}{V^2}$
  - c.  $\frac{an^2}{V^2}$
  - d. nb

[IIT 2009]

## ANSWERS

## Straight Objective Type Questions

- |              |              |              |              |              |              |              |              |              |              |
|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| <b>1.</b> c  | <b>2.</b> a  | <b>3.</b> c  | <b>4.</b> d  | <b>5.</b> a  | <b>6.</b> b  | <b>7.</b> d  | <b>8.</b> c  | <b>9.</b> b  | <b>10.</b> d |
| <b>11.</b> d | <b>12.</b> d | <b>13.</b> b | <b>14.</b> a | <b>15.</b> c | <b>16.</b> c | <b>17.</b> d | <b>18.</b> a | <b>19.</b> b | <b>20.</b> c |
| <b>21.</b> c | <b>22.</b> d | <b>23.</b> d | <b>24.</b> c | <b>25.</b> c | <b>26.</b> a | <b>27.</b> b | <b>28.</b> c | <b>29.</b> b | <b>30.</b> c |
| <b>31.</b> d | <b>32.</b> d | <b>33.</b> b | <b>34.</b> b | <b>35.</b> d | <b>36.</b> a | <b>37.</b> c | <b>38.</b> c | <b>39.</b> a | <b>40.</b> b |
| <b>41.</b> c | <b>42.</b> b | <b>43.</b> c | <b>44.</b> d | <b>45.</b> a | <b>46.</b> a | <b>47.</b> d | <b>48.</b> d | <b>49.</b> b | <b>50.</b> a |

## **Brainteasers Objective Type Questions**

- |              |              |              |              |              |              |              |              |              |              |
|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| <b>51.</b> b | <b>52.</b> b | <b>53.</b> c | <b>54.</b> b | <b>55.</b> b | <b>56.</b> c | <b>57.</b> c | <b>58.</b> d | <b>59.</b> a | <b>60.</b> a |
| <b>61.</b> d | <b>62.</b> a | <b>63.</b> b | <b>64.</b> B | <b>65.</b> d | <b>66.</b> b | <b>67.</b> a | <b>68.</b> c | <b>69.</b> d | <b>70.</b> c |
| <b>71.</b> b | <b>72.</b> c | <b>73.</b> a | <b>74.</b> c | <b>75.</b> d | <b>76.</b> b | <b>77.</b> c | <b>78.</b> c | <b>79.</b> d | <b>80.</b> a |
| <b>81.</b> a | <b>82.</b> c | <b>83.</b> b | <b>84.</b> d | <b>85.</b> b | <b>86.</b> b | <b>87.</b> d | <b>88.</b> c | <b>89.</b> d | <b>90.</b> a |
| <b>91.</b> c | <b>92.</b> a | <b>93.</b> a | <b>94.</b> b | <b>95.</b> c | <b>96.</b> b |              |              |              |              |

## **Multiple Correct Answer Type Questions**

- |                     |                     |                     |                        |                     |                     |
|---------------------|---------------------|---------------------|------------------------|---------------------|---------------------|
| <b>97.</b> c, d     | <b>98.</b> b, c, d  | <b>99.</b> a, b, c  | <b>100.</b> a, c, d    | <b>101.</b> a, b    | <b>102.</b> a, b, d |
| <b>103.</b> b, d    | <b>104.</b> b, c, d | <b>105.</b> b, c    | <b>106.</b> b, c       | <b>107.</b> a, c    | <b>108.</b> b, c, d |
| <b>109.</b> a, b    | <b>110.</b> b, c, d | <b>111.</b> c, d    | <b>112.</b> c, d       | <b>113.</b> a, c    | <b>114.</b> a, d    |
| <b>115.</b> a, d    | <b>116.</b> a, b, d | <b>117.</b> a, c    | <b>118.</b> a, b, c, d | <b>119.</b> a, b    | <b>120.</b> a, b, c |
| <b>121.</b> a, b, c | <b>122.</b> b, c, d | <b>123.</b> a, c, d | <b>124.</b> b, c       | <b>125.</b> a, c    | <b>126.</b> b, c    |
| <b>127.</b> a, b, c | <b>128.</b> a, c    | <b>126.</b> b, d    | <b>130.</b> b, c       | <b>131.</b> a, b, c | <b>132.</b> b, c, d |
| <b>133.</b> b, d    | <b>134.</b> c, d    | <b>135.</b> a, c    | <b>136.</b> a, b, d    | <b>137.</b> b, c, d | <b>138.</b> a, c    |
| <b>139.</b> a, b    | <b>140.</b> b, c    |                     |                        |                     |                     |

## Linked-Comprehension Type Questions

### Comprehension 1

141. b      142. c      143. b

### Comprehension 2

144. a      145. c      146. c

### Comprehension 3

147. b      148. c      149. d

### Comprehension 4

150. b      151. c      152. b      153. a      154. c

### Comprehension 5

155. b      156. b      157. a

## Assertion Reason Type Questions

158. a      159. b      160. c      161. a      162. d

163. b      164. c      165. e      166. c      167. a

168. d      169. c      170. a      171. e      172. a

173. a      174. b      175. a      176. a      177. d

178. a      179. a      180. a      181. a      182. a

## Matrix-Match Type Questions

183. A-(r), B-(p), C-(p, q), D-(s, t)

184. A-(q), B-(p, r), C-(p), D-(r, s)

185. A-(q, s), B-(p), C-(r), D-(t)

186. A-(s), B-(p), C-(r), D-(q)

187. A-(s), B-(q), C-(r), D-(p)

188. A-(s), B-(p), C-(q), D-(r)

189. A-(r), B-(q), C-(s), D-(p)

190. A-(s), B-(q), C-(p), D-(r)

191. A-(r), B-(q), C-(s), D-(p)

192. A-(s), B-(r), C-(q), D-(p)

193. A-(t), B-(p), C-(q), D-(r)

194. A-(p, s), B-(r), C-(p, q), D-(p, s)

## The IIT-JEE Corner

195. b      196. d      197. b      198. c

199. b      200. c      201. d      202. d

203. b      204. c      205. a      206. a

207. b, c, d      208. b

## Hints and Explanations

### Straight Objective Type Questions

- According to Boyle's law

$$PV = \text{Cosntant.}$$

By differentiating this equation, we have

$$PdV = VdP = 0$$

$$VdP = -PDV$$

$$\frac{dP}{P} = -\frac{dV}{V}$$

- At very low pressure, the real gas approaches ideal behaviour.
- Plot is a horizontal line. Hence slope = 0.
- $PV = RT$  or  $V = RT/P$ . Greater the value of  $T/P$ , greater is the volume.
- As its molecular weight is maximum so it will have minimum average speed.
- Lower the density of the gas, faster it will be filled As  $H_2$  has lowest density, it will be filled first.

## 2.48 ■ Gaseous and Liquid States

17. Density =  $\frac{\text{mass}}{\text{Volume}}$

Due to ideal behaviour at a given temperature and pressure volume and molar mass are same so they have same vapour density.

18.  $u = \sqrt{(3RT/M)}$ .

At constant temperature,  $u \propto \sqrt{(1/M)}$ .

As  $H_2$  has least molecular mass,  $u$  will be maximum for  $H_2$ .

19. As  $d \propto$  pressure

$\propto 1/\text{temperature}$

20. As kinetic energy is  $\propto$  temperature

So it will become four times as temperature is increased from 300 K to 1200 K.

21. As liquification of gas  $\propto$  'a'

i.e.,  $NH_3 > CH_4 > N_2 > O_2$

26. Average kinetic energy depends only on temperature and does not depend upon the nature of the gas.

28. The collision between the molecules to be perfectly elastic because the temperature remains constant irrespective of collision.

29. The temperature at which a real gas behaves like an ideal gas is called Boyle's temperature or Boyle's point.

31. As the condition of constant pressure or constant volume is not mentioned so the gas may be monoatomic or diatomic.

36. Average translational kinetic energy of gas molecules =  $3/2 kT$ .

37. According to Charles' law,

At constant pressure,  $V/T = \text{constant}$

i.e.,  $V = kT$ .

So plot of  $V$  vs  $T$  is a straight line passing through the origin.

38. As  $CO_2$  has lowest molecular mass here so it will have highest average speed.

39. It represents most probable velocity given by  $\sqrt{2RT/M}$ .

40. K.E. =  $\frac{3}{2} nRT$

K.E. =  $\frac{3}{2} RT$

When  $n = 1$

42. Van der Waal's constant 'b' is four times the actual volume of 1 mole molecules i.e.,  $4VN_0$

44. Van der Waal's equation for one mol of a gas is given as

$$[P + a/V^2] (V - b) = RT$$

where  $b$  is volume correction. It arises due to finite size of gaseous molecules.

48.  $a = \frac{PV^2}{n^2}$  (atm L<sup>2</sup> mol<sup>-2</sup>)

$b = L \text{ mol}^{-1}$

So  $\frac{a}{b} = \left( \frac{\text{atm L}^2 \text{ mol}^{-2}}{L \text{ mol}^{-1}} \right) = \text{atm L mol}^{-1}$

### Brainteasers Objective Type Questions

52. Using Graham's law,  $TO_2$  is 20 seconds.

53. Initially, partial pressures were equal.

As  $r \propto \sqrt{(1/d)}$  or  $\sqrt{(1/M)}$ , therefore amounts diffused out in the same time will be  $H_2 > CH_4 > SO_2$ . So amounts left will be  $H_2 < CH_4 < SO_2$  or  $SO_2 > CH_4 > H_2$ .

Thus,  $\rho(SO_2) > \rho(CH_4) > \rho(H_2)$ .

55. At constant temperature

$V = K/P$  (Boyle's law)

$So P = K/V$

As such, a graph plotted between  $P$  and  $1/V$  is linear at a constant temperature.

56.  $\mu_1/\mu_2 = \sqrt{(T_1 M_2 / M_1 T_2)}$

=  $\sqrt{(50 \times 32/800 \times 2)}$

= 1

58. Applying Dalton's law

$$PH_2 = \frac{W/2}{W/2 + W/30} \times P_{\text{total}}$$

On solving

$$PH_2 = 15/16 P_{\text{total}}$$

59. At the same temperature, oxygen and hydrogen molecules will have the same average energy; weight of  $H_2$  molecules is  $1/16$  of  $O_2$  molecules.

60.  $r_{CH_4}/r_x = \sqrt{(Mx/MCH_4)}$

$2 = \sqrt{(Mx/16)}$

$Mx = 64$

61. Molar volume ( $M^3$ ) at STP are

$NH_3 : 0.022094$

$$\text{O}_2 : 0.022392$$

$$\text{N}_2 : 0.022403$$

$$\text{H}_2 : 0.022432$$

$\text{NH}_3$  has a dipole moment. Dipole-dipole interaction, most likely plays its role in reducing the volume.

62.  $V_1/V_2 = \sqrt{T_1/T_2}$

$$0.3/V_2 = \sqrt{(300/1200)}$$

$$V_2 = 0.6 \text{ m/sec}$$

63.  $U_{\text{rms}} = \sqrt{3RT/M}$

$$\frac{U_{\text{rms}}(\text{H}_2)_{50\text{ K}}}{U_{\text{rms}}(\text{O}_2)_{800\text{ K}}}$$

$$= \sqrt{[(\text{TH}_2/\text{TO}_2) \times (\text{MO}_2/\text{MH}_2)]}$$

$$= \sqrt{[(50/800) \times (32/2)]}$$

$$= 1$$

64. As ammonia will have more diffusion rate than  $\text{NH}_3$  due to less molecular weight.

66. Applying Dalton's law

$$P\text{H}_2 = \frac{W/2}{W/2 + W/16} \times P_{\text{total}}$$

On solving

$$P\text{H}_2 = 8/9 P_{\text{total}}$$

67. At constant pressure, temperature, and volume, the number of moles of  $\text{CCl}_4$  and  $\text{O}_2$  will be same. But the molar mass of  $\text{CCl}_4$  is approximately 5 times than that of  $\text{O}_2$ .

68.  $U_{\text{rms}} : U_{\text{av}}$

$$\sqrt{3RT/M} : \sqrt{8RT/\pi M}$$

$$\sqrt{3} : \sqrt{8/\pi} = 1.086 : 1$$

69. Pressure exerted by oxygen will proportional to mole fraction of  $\text{O}_2$ .

$$\text{Mole fraction of O}_2 = \frac{W/32}{W/16 + W/32} = 1/3$$

70. Given  $P$  (pentane) = 440 mm

$$P(\text{hexane}) = 120 \text{ mm}$$

From Dalton's law of partial pressure

$$P(\text{total}) = P(\text{pentane}) + P(\text{hexane})$$

$$= (440 + 120) \text{ mm} = 560 \text{ mm}$$

mole fraction,

$$X(\text{pentane}) = 440/560 = 0.786$$

72. According to Boyle's law

$$PV = \text{Cosntant.}$$

By differentiating this equation, we have

$$PdV = VdP = 0$$

$$VdP = -PDV$$

$$\frac{dP}{P} = -\frac{dV}{V}$$

73.  $v_{\text{rms}} = \sqrt{3RT/M}$

$$(30 R^{1/2})^2 = \frac{3RT}{M}$$

$$900 R = \frac{3R \times 300}{M}$$

On solving, we get

$$M = 1 \text{ g mol}^{-1} = 0.001 \text{ kg mol}^{-1}$$

74.  $M = \frac{w}{V} \cdot \frac{RT}{P} = d \frac{RT}{P}$

$$\text{i.e., } M = \frac{1.964 \times 10^{-3} \times 82.1 \times 273}{1}$$

= 44 i.e., the gas is  $\text{CO}_2$

75.  $r_a/r_b = 2/1 = \sqrt{(M_b/M_a)}$

$$V_{\text{rms}} \propto \sqrt{T/M}$$

$$(\text{As } V_{\text{rms}} = \sqrt{3RT/M})$$

$$V_{\text{rms (a)}}/V_{\text{rms (b)}} = \sqrt{[(T_a/T_b) \times (M_b/M_a)]}$$

$$= \frac{2}{1} \times \frac{\sqrt{2}}{1} = \frac{2\sqrt{2}}{1}$$

$$2\sqrt{2} : 1$$

76. According to Boyle's law

$$P_A \times V_A = 0.4 P_A \times V_B$$

$$100 \times P_A = 0.4 P_A \times V_B$$

$$V_B = 250 \text{ cc}$$

Before opening the stopcock, volume of gas in bulb B must be  $(250 - 100) = 150 \text{ ml.}$

77. As  $V_{\text{av}} \propto \sqrt{1/M}$

$$\text{So } \frac{V(\text{SO}_2)}{V(\text{gas})} = \sqrt{[M(\text{gas})/M(\text{SO}_2)]}$$

On solving

$$M(\text{gas}) = 16 \text{ i.e., CH}_4$$

## 2.50 ■ Gaseous and Liquid States

78.  $\frac{PV}{T} = \frac{P'V'}{T'}$ .

Here  $V' = 2V$ ,  $T' = 2T$

$$\frac{PV}{T} = \frac{P' \times 2V}{2T} \text{ or } P = P'$$

i.e., pressure remains same.

80. 6.4 g of  $\text{SO}_2$  at N.T.P. (i.e., at 0°C temperature and 1 atm pressure) occupies a volume of 2.24 lit.

64 g of  $\text{SO}_2$  i.e., 1 mole  $\text{SO}_2$  at N.T.P. occupies a volume of 22.41 lit.

now 1 mole of an ideal gas occupies 22.4 litre at N.T.P. condition.

Therefore  $\text{SO}_2$  acts as an ideal gas.

81. Work done is reversible process is maximum. Thus  $T_2 \ll T_1$  in reversible process or  $T_{\text{rev}} \ll T_{\text{irr}}$

82.  $M_{\text{mix}} = M_1 X_1 + M_2 X_2$

$$= 17 \times \frac{20}{100} + 34 \times \frac{80}{100} = 30.6$$

$$\text{Vapour density of mixture} = \frac{30.6}{2} = 15.6$$

83. When the value of  $Z < 1$ , it is due to attractive forces between molecules, At high pressure, when  $Z > 1$ , it is due to repulsive forces between electron clouds of the molecules of gases

84. (c) is not possible as gas is same ( $\text{H}_2$ ).

(d) is possible

$$\frac{t_1}{t_2} = \frac{\sqrt{M_1}}{\sqrt{M_2}}$$

$$\frac{5}{t_2} = \frac{\sqrt{2}}{\sqrt{32}}$$

$$t_2 = 20 \text{ sec.}$$

86. Let the mass of methane and oxygen is w

$$\text{Mole fraction of oxygen} = \frac{w/32}{w/32 + w/16}.$$

$$= \frac{1/32}{1/32 + 1/16} = \frac{1/32}{3/32} = 1/3$$

Let the total pressure be P.

The pressure exerted by oxygen (partial pressure) =  $X_{\text{O}_2} \times P_{\text{total}} = P \times 1/3$

87. Pressure of helium = 8 bar

Pressure of methane = 2 bar

$$\frac{r(\text{He})}{r(\text{CH}_4)} = \frac{P_1}{P_2} \frac{\sqrt{M_{\text{CH}_4}}}{\sqrt{M_{\text{He}}}} \rightarrow \frac{\sqrt{M_{\text{CH}_4}}}{\sqrt{M_{\text{He}}}}$$

$$= 8/2 \frac{\sqrt{16}}{\sqrt{4}}$$

$$= 8 : 1$$

88.  $\frac{r_{\text{He}}}{r_{\text{CO}}} = \frac{\sqrt{M_{\text{CO}}}}{\sqrt{M_{\text{He}}}} = \sqrt{(28/4)} = 2.65$

$$r_{\text{CO}} = \frac{r_{\text{He}}}{2.65} = \frac{6.4}{2.65} = 2.4 \text{ mole/hour}$$

$$t = \frac{10}{2.4} \approx 4.2 \text{ hours}$$

89.  $\text{SO}_3 = \text{O}_2 = w \text{ g}$

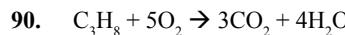
$$n(\text{SO}_3) = w/80$$

$$n(\text{O}_2) = w/32$$

The partial pressures will be in the ratio of their moles.

$$\text{So, } p(\text{SO}_3) : p(\text{O}_2) = \frac{w}{80} : \frac{w}{32}.$$

$$\frac{1}{80} : \frac{1}{32} = \frac{1}{5} : \frac{1}{2} = 2 : 5$$



$$1 \quad 5 \qquad \qquad \qquad 3 \qquad \qquad \qquad 4 \qquad \qquad \text{volume}$$

So 1 volume or 1 litre of propane requires to 5 volume or 5 litre of  $\text{O}_2$  to burn completely.

92. The average translational K.E. of one molecule of an ideal gas is as follows:

$$K_t = \frac{\text{K.E.}}{N_A} = \frac{3/2 RT}{N_A} = \frac{3}{2} KT$$

When  $R/N_A$  = Boltzmann constant

i.e.,  $E_t \propto T$

Thus, at constant temperature K.E. of molecules remains same.

93. According to Boyle's law, Pressure is inversely proportional to volume.

$$\text{i.e., } P = \alpha \frac{1}{V}$$

or  $PV = \text{constant}$

$$\text{As, } P_1 V_1 = P_2 V_2$$

$$P_2 = P \times \frac{V}{1.1V}$$

$P_2 = 0.9 \times P$  (i.e., 10% decrease in pressure).

### Multiple Correct Answer Type Questions

100. As most probable velocity increases and fraction of molecule possessing most probable velocity decreases.
101. As temperature is constant pressure decreases during expansion while kinetic energy remains same.
115. Reversible adiabatic expansion lowers the temperature hence facilitates the liquefaction of gas. A gas can be liquefied below the critical temperature by increasing the pressure.
129. As one mole of a gas has always  $N_0$  number of molecules and kinetic energy depends only on temperature.
139.  $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$   
 $(50 - X) \quad X \quad 0$

### Case 1

Suppose  $H_2$  is the limiting reagent

So after the reaction volume of  $O_2$  remains

$$= X - \frac{(50 - X)}{2} = \frac{3X - 50}{2}$$

$$\frac{3X - 50}{2} = 10$$

$$X = 70/3 = 23.33$$

$$\text{So mole fraction of } H_2 = \frac{(50 - 23.33)}{50}$$

$$= 0.534$$

### Case 2

Suppose  $O_2$  is the limiting reagent

After the reaction volume of  $H_2$  remains

$$= (50 - X - 2X) = (50 - 3X)$$

$$\text{So } (50 - 3X) = 10$$

$$X = 40/3 = 13.33$$

Mole fraction of  $H_2$  in the original mixture

$$= \frac{(50 - 13.33)}{50} = 0.733$$

### Linked-Comprehension Type Questions

#### Comprehension 3

147.  $\frac{r_{\text{vapour}}}{r_{O_2}} = \sqrt{(M O_2 / M_{\text{vapour}})}$

$$1.33 = \sqrt{(32 / M_{\text{vapour}})}$$

$$M_{\text{vapour}} = 18$$

148. As volume of vapour ( $V_{\text{real}}$ ) = 1 m<sup>3</sup>

$$= 1000 \text{ litre.}$$

$$\text{Mass of the vapour} = 0.36 \text{ kg} = 360 \text{ gm.}$$

$$\text{So moles of the vapour (n)}$$

$$= \frac{360}{18} = 20$$

$$\text{As } PV_{\text{ideal}} = nRT$$

$$V_{\text{ideal}} = \frac{nRT}{P}$$

$$= \frac{20 \times 0.082 \times 500}{1} = 820 \text{ litre}$$

$$\text{Hence compressibility factor (Z)}$$

$$= \frac{V_{\text{real}}}{V_{\text{ideal}}} = \frac{1000}{820} = 1.22$$

149. As  $(K.E.)_{\text{Av}} = \frac{3}{2} \frac{nRT}{N_0}$

$$= \frac{3}{2} \times \frac{1 \times 8.314 \times 1000}{6.02 \times 10^{23}}$$

$$= 2.07 \times 10^{-20} \text{ J.}$$

#### Comprehension 4

150. As critical temperature,  $T_c = \frac{8a}{27Rb}$ .

So greater is the value of (a/b), more is the critical temperature of gas

For gas X,  $T_c$  will be maximum,

$$T_c = \frac{8a}{27Rb}.$$

a/b for X = 6/0.025 = 240; for all other gases (a/b) is lesser.

151.  $(P + a \frac{n^2}{V^2})(V - nb) = nRT$

For one mole gas

$$(P + \frac{a}{V^2})(V - b) = RT$$

At high pressure,

$$(P + \frac{a}{V^2}) \approx P$$

$$\text{So } P(V - b) = RT$$

$$PV = RT + Pb$$

152. As value of 'b' for hydrogen is 0.021 dm<sup>3</sup> mol<sup>-1</sup> while 'b' for He is 0.019 dm<sup>3</sup> mol<sup>-1</sup>.

## 2.52 ■ Gaseous and Liquid States

153.  $T_b = \frac{a}{R_b} = \frac{3.592}{0.0821 \times 0.0427}$

$$= 1024.7 \text{ K} = 752^\circ\text{C}$$

So  $\text{CO}_2$  behaves ideal in nature in the temperature range  $752 \pm t^\circ\text{C}$ .

### Assertion-Reason Type Questions

160. These gases have very low inversion temperature.
162. All molecules of the ideal gas does not move with same speed their average speed is same.
164. The temperature of which the Joule-Thomson coefficient becomes zero is called Joule-Thomson inversion temperature.

### Matrix-Match Type Questins

194. (A)  $Z = \frac{PV_m}{RT}$  at high pressure and low temp.

Equation  $(P + an^2/V^2)(V - nb) = nRT$  reduces to  $P(V - nb) = nRT$ .

(B) For hydrogen gas value of  $Z = 1$  at  $P = 0$  and it increase continuously on increasing pressure.

(C)  $\text{CO}_2$  molecules have larger attractive forces, under normal conditions.

(D)  $Z = \frac{PV_m}{RT}$ ,

at very large molar volume  $Z \neq 1$ .

### The IIT-JEE Corner

196. More the dipole moment more is the critical temperature.

197. At constant temperature

$$V = K/P \text{ (Boyle's law)}$$

$$\text{So } P = K/V$$

As such, a graph plotted between  $P$  and  $1/V$  is linear at a constant temperature.

198.  $1\text{L} = 1000 \text{ mL} = 1000 \text{ cm}^3$

$$\text{mass} = \text{density} \times \text{volume}$$

$$= (0.0006 \text{ g cm}^{-3}) \times (1000 \text{ cm}^3)$$

$$= 0.6 \text{ g}$$

$$\text{as } 18 \text{ g of water} = 18 \text{ cm}^3$$

$$\text{so } 0.6 \text{ g of water} = 0.6 \text{ cm}^3$$

hence actual volume occupied by molecules

$$= 0.6 \text{ cm}^3$$

199.  $Z = PV/nRT$

$$\text{Given } Z < 1$$

$$PV/nRT < 1 \text{ or } PV < nRT$$

$$(1 \text{ atm}) \times V < 1 \text{ mol} \times (0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})$$

$$Vm < 0.0821 \times 273 \text{ L}$$

$$Vm < 22.4 \text{ L}$$

200.  $\mu_{H_2}/\mu_{N_2} = \sqrt{[(T_{H_2}/M_{H_2}) \times (M_{N_2}/T_{N_2})]}$

$$\sqrt{7} = \sqrt{(T_{H_2} \times 28/T_{N_2} \times 2)} = T_{H_2} \times 14/N_2$$

$$TN_2 = 2 T_{H_2}$$

$$\text{so } TN_2 > T_{H_2}$$

201. As  $u = \sqrt{(3PV/m \times N_0)} = \sqrt{(3P/N_0) \cdot (1/d)}$

$$\text{So } u \propto 1/\sqrt{d}$$

202. Volume of 1 mole of an ideal gas at 273 K and 1 atm is 22.4 L. Volume at 373 K and 1 atm pressure will be

$$V = \frac{RT}{P} = \frac{0.082 \times 373}{1}$$

$$= 30.58 \text{ L} = 30.6 \text{ L}$$

203. For positive deviation

$$PV/nRT > 1$$

$$PV = nRT + nPb$$

$$PV/nRT = 1 + Pb/RT$$

$$PV/nRT > 1.$$

204. RMS of one mole of monoatomic gas is

$$Urms = \sqrt{(3RT/M)}$$

$$\text{Average K.E. is } E = \frac{3}{2} RT \text{ or } 2E = 3RT$$

$$Urms = \sqrt{(2E/M)}$$

205. According to Graham's diffusion law,

$$\frac{r(\text{He})}{r(\text{CH}_4)} = \frac{\sqrt{M(\text{CH}_4)}}{\sqrt{M(\text{He})}}$$

$$M(\text{CH}_4) = 12 + 4 = 16$$

$$M(\text{He}) = 4$$

$$\frac{r(\text{He})}{r(\text{CH}_4)} = \frac{\sqrt{16}}{4} = 2.$$

207. See Text part.

208. See Text part.

## Numericals For Practice

- Find volume of  $\text{O}_2$  that can be prepared at 333 K and 1 atm pressure due to decomposition of 20 gm of  $\text{H}_2\text{O}_2$ .
  - 4.01 lit
  - 8.04 lit
  - 2.01 lit
  - 6.03 lit
- 50 gm  $\text{H}_2\text{O}$  on electrolysis give  $\text{H}_2$ ,  $\text{O}_2$  which are enclosed in a vessel of 60 litre at 290 K. Find partial pressure of each gases.
  - 1.102 and 0.551 atm
  - 0.551 and 1.102 atm
  - 1.421 and 1.612 atm
  - 0.331 and 0.872 atm
- One litre flask having vapours of  $\text{CH}_3\text{OH}$  at a pressure of 1 atm and 298 K was evacuated till the pressure was 0.0001 mm. Now how many moles of  $\text{CH}_3\text{OH}$  will be left in flask?
  - $6.02 \times 10^{21}$
  - $3.24 \times 10^{15}$
  - $3.24 \times 10^{18}$
  - $6.02 \times 10^{15}$
- In the study of pressure volume relationship, the following data were collected at room temperature
 

	(I)	(II)	(III)	(IV)
V (L)	10.5	5.25	3.5	3.3
P (atm)	1	2	3.0	3.5

 In which observation the volume was not recorded correctly?
  - I only
  - II and III
  - IV only
  - III and IV
- An iron cylinder contains He at a pressure of 250 kPa at 300 K. This cylinder can withstand a pressure of  $1 \times 10^6$  Pa. The room in which cylinder is placed catches fire. Predict which is correct statements about cylinder (melting point of cylinder 1800 K)?
  - Will melt and burst
  - Neither melt nor burst
  - Will melt but not burst
  - Can not be predicted
- A gas cylinder containing cooling gas can withstand pressure of 14.9 atmosphere. The pressure gauge of the cylinder indicate 12 atm at 27°C due to a sudden fire in the building, its temperature starts rising. At what temperature will the cylinder explode?
  - 362.5 K
  - 390 K
  - 372.5 K
  - 426 K
- When 18 g of  $\text{H}_2\text{O}$  is heated at 400 K and 2 atm pressure  $\text{H}_2$  gas is evolved. Find the volume it will occupy. If the ratio of H : O by weight in  $\text{H}_2\text{O}$  is 1 : 8. One g of  $\text{H}_2$  occupy 11.2 litre at N.T.P?
  - 22.4 lit
  - 11.2 lit
  - 15.4 lit
  - 16.4 lit
- A vessel of volume  $0.02 \text{ m}^3$  contain a mixture of  $\text{H}_2$  and He at 320 K and  $41.5 \times 10^4 \text{ N m}^{-2}$ . The mass of the mixture is  $10^{-2}$  kg. Find the mass of  $\text{H}_2$  and He in mixture respectively.
  - 2.48 g, 7.52 g respectively
  - 7.52 g, 2.48 g respectively
  - 3.26 g, 6.74 g respectively
  - 4.48 g, 5.52 g respectively
- If at a distance of 100 miles above earth the temperature is  $-160^\circ\text{C}$  and pressure of atmosphere is  $2 \times 10^{-6}$  mm. What will be the number of moles at this altitude for 2 ml of a gas?
  - $4.36 \times 10^{-11}$
  - $11.72 \times 10^{-9}$
  - $5.66 \times 10^{-13}$  moles
  - $8.42 \times 10^5$  moles
- If at a certain temperature, a student wants to decrease the volume of a gas by 5 %. How much pressure should he must increase for it?
  - 15%
  - 8.34%
  - 5.26%
  - 56%

## 2.54 ■ Gaseous and Liquid States

11. The volume of average adult lung was found to be 6 litre nearly at 98.4°F during expansion. If the pressure of O<sub>2</sub> in inhaled air is found to be 168 mm of Hg. What will be the mass of O<sub>2</sub> needed to occupy the lung at this temperature?
- a. 1.67 g      b. 2.07 g  
c. 8.34 g      d. 0.923 g
12. An LPG cylinder at 300 K has 15 kg of butane at 10 atmosphere pressure. After a leakage it was found that its pressure fell down to 8 atmosphere in one day. The gas leaked in 3 days will be
- a. 5 kg      b. 6 kg  
c. 3 kg      d. 9 kg
13. A student has a flask containing air. He heated it from 300 K to 500 K. What % of air escaped to the atmosphere will be?
- a. 40%      b. 50%  
c. 30%      d. 100%
14. A manometer is connected to a gas containing bulb. If the open arm read 43.6 cm, while the arm joined to bulb reads 15.5 cm. If the barometer reads a pressure of 742 mm of Hg. What will be pressure of gas in bar?
- a. 1.06 bar      b. 4.32 bar  
c. 1.36 bar      d. 9.82 bar
15. Pressure of 1 g of an ideal gas 'X' at 300 K is 2 bar. When 2 g of another ideal gas 'Y' is added in same flask at same temperature, the pressure is found to be 3 bar. What will be the relationship between M<sub>X</sub> and M<sub>Y</sub> (masses of X and Y)?
- a. M<sub>Y</sub> = 4 M<sub>X</sub>      b. M<sub>Y</sub> =  $\frac{1}{2}$  M<sub>X</sub>  
c. M<sub>X</sub> = 3 M<sub>Y</sub>      d. M<sub>X</sub> = 4 M<sub>Y</sub>
16. At 273 K, it is found that density of N<sub>2</sub> at 5 bar is equal to a gaseous oxide at 2 bar. What will be the molecular weight of gaseous oxide?
- a. 60      b. 68.5  
c. 82      d. 70
17. A student found at the top of mountain and bottom of it, the values of temperature and pressure respectively are
- |       |        |        |
|-------|--------|--------|
|       | Bottom | Top    |
| Temp. | 30°C   | 0°C    |
| Pr.   | 760 mm | 710 mm |
- The ratio of density at top and bottom is
- a. 1 : 1.04      b. 1.04 : 1  
c. 2 : 1      d. 1 : 3
18. Find volume occupied by 5 g C<sub>2</sub>H<sub>2</sub> at 50°C and 740 mm pressure?
- a. 5.23 lit      b. 3.23 lit  
c. 6.26 lit      d. 8.23 lit
19. 0.55 lit of a gas is collected over water at 298 K and 755 mm pressure. Now gas is saturated with water vapours. Find volume of gas at NTP in dry condition. Vapour pressure of H<sub>2</sub>O at 298 K is 23.8 mm.
- a. 0.625 lit      b. 0.485 lit  
c. 0.373 lit      d. 0.175 lit
20. 100 cc of methane at 600 mm of Hg pressure and 2000 cc of oxygen at 400 mm of Hg pressure were enclosed in a three litre flask. Calculate the total pressure when the temperature is constant.
- a. 268.4 mm      b. 286.7 mm  
c. 362.1 mm      d. 270.5 mm
21. A mixture of gas in a cylinder has 20% CO<sub>2</sub>, 15% O<sub>2</sub> and 65% N<sub>2</sub> at 760 mm and 300 K. The partial pressure of each gas will be respectively?
- a. 152, 114 and 494 mm  
b. 494, 114 and 152 mm  
c. 114, 494 and 152 mm  
d. 210, 214 and 336 mm
22. Ammonia and the hydrogen chloride gases are introduced simultaneously at the ends of a 90 cm tube. At what distance ammonium chloride is formed from the end at which HCl is introduced?
- a. 55.53      b. 182.5 cm  
c. 36.51 cm      d. 18.25 cm
23. Find the relative rates of diffusion of <sup>235</sup>UF<sub>6</sub> and <sup>238</sup>UF<sub>6</sub> respectively?
- a. 1 : 1.526      b. 1.526 : 1  
c. 1 : 1.0023      d. 1.0043 : 1
24. Three similar balloons were filled respectively with O<sub>2</sub>, CO<sub>2</sub> and Cl<sub>2</sub> under similar conditions. In ten hours one-half the CO<sub>2</sub> had escaped. How much of each of the other gases escaped during the same period of time?
- a. O<sub>2</sub> = 0.6; Cl<sub>2</sub> = 0.4  
b. O<sub>2</sub> = 0.4; Cl<sub>2</sub> = 0.6  
c. O<sub>2</sub> = 0.8; Cl<sub>2</sub> = 0.2  
d. O<sub>2</sub> = 0.0.2; Cl<sub>2</sub> = 0.6
25. A porous container was filled with equal amounts of oxygen and a gas of unknown molecular weight.

The oxygen escaped 1.77 times faster than the unknown gas. Calculate the molecular weight of the unknown gas.

- |              |               |
|--------------|---------------|
| <b>a.</b> 44 | <b>b.</b> 99  |
| <b>c.</b> 66 | <b>d.</b> 189 |

**26.** If the temperature of 1 mole of a gas is increased by 50 °C, calculate the change in kinetic energy of the system.

- |                   |                    |
|-------------------|--------------------|
| <b>a.</b> 62.32 J | <b>b.</b> 6.235 J  |
| <b>c.</b> 623.5 J | <b>d.</b> 6235.0 J |

**27.** Find the temperature at which H<sub>2</sub> at one atm pressure has the same root mean square velocity similar to O<sub>2</sub> at N.T.P.

- |                   |                    |
|-------------------|--------------------|
| <b>a.</b> -255 K  | <b>b.</b> 325 K    |
| <b>c.</b> 17.06 K | <b>d.</b> -17.06 K |

**28.** If the temperature of 1 mole of a gas is increased by 50°C, calculate the ratio of average velocity of SO<sub>2</sub> to CH<sub>4</sub>:

- |                 |                 |
|-----------------|-----------------|
| <b>a.</b> 1 : 2 | <b>b.</b> 3 : 4 |
| <b>c.</b> 2 : 3 | <b>d.</b> 1 : 6 |

**29.** The van der Waals constant b for helium gas is 0.02337 litre mole<sup>-1</sup>. Calculate the approximate diameter of the helium molecule assuming the molecule to be spherical.

- |                                     |
|-------------------------------------|
| <b>a.</b> $6.22 \times 10^{-8}$ cm. |
| <b>b.</b> $5.66 \times 10^{-8}$ cm. |
| <b>c.</b> $26.6 \times 10^{-8}$ cm. |
| <b>d.</b> $2.66 \times 10^{-8}$ cm. |

**30.** The average velocity of an ideal gas molecule at 27°C is 0.3 m/s. The average velocity at 927°C will be

- |                   |                   |
|-------------------|-------------------|
| <b>a.</b> 0.6 m/s | <b>b.</b> 0.3 m/s |
| <b>c.</b> 0.9 m/s | <b>d.</b> 3.0 m/s |

**31.** The ratio of V<sub>r.m.s.</sub> and V<sub>av.</sub> at a particular temperature is

- |                     |                     |
|---------------------|---------------------|
| <b>a.</b> 1.086 : 2 | <b>b.</b> 1.086 : 1 |
| <b>c.</b> 1 : 1.086 | <b>d.</b> 2 : 1.086 |

**32.** Using van der waal's equation find the pressure of 15 mol of Neon at 303 K in 1200 ml vessel. (Given: a = 0.2107 L<sup>2</sup> atm/mol<sup>2</sup>, b = 0.0171 L/mol)

- |                     |                    |
|---------------------|--------------------|
| <b>a.</b> 13.23 atm | <b>b.</b> 31.4 atm |
| <b>c.</b> 21.34 atm | <b>d.</b> 7.12 atm |

**33.** If 'X' is the volume of one molecule of a gas under given conditions then van der waal's constant 'b' is

- |                    |                         |
|--------------------|-------------------------|
| <b>a.</b> 4X       | <b>b.</b> $4X/N_0$      |
| <b>c.</b> $4X N_0$ | <b>d.</b> None of these |

**34.** Find the temperature at which the average speed of Hydrogen = that of oxygen at 320 K.

- |                 |                 |
|-----------------|-----------------|
| <b>a.</b> 200 K | <b>b.</b> 300 K |
| <b>c.</b> 100 K | <b>d.</b> 20 K  |

**35.** Find the pressure exerted by 22 gm of CO<sub>2</sub> in 0.5 dm<sup>3</sup> at 298.15 K using van der Waal's equation if

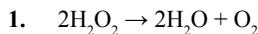
$$a = 363.76 \text{ kPa dm}^6 \text{ mol}^{-2} \text{ and } b = 42.67 \text{ cm}^3 \text{ mol}^{-1}$$

- |                      |                       |
|----------------------|-----------------------|
| <b>a.</b> 2.2255 kPa | <b>b.</b> 222.55 kPa  |
| <b>c.</b> 2225.5 kPa | <b>d.</b> 0.22255 kPa |

### ANSWER KEYS

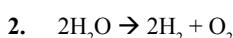
Q.	Ans.								
1.	b	2.	a	3.	b	4.	c	5.	b
6.	c	7.	d	8.	a	9.	c	10.	c
11.	a	12.	d	13.	a	14.	c	15.	a
16.	d	17.	b	18.	a	19.	b	20.	b
21.	a	22.	c	23.	d	24.	a	25.	b
26.	c	27.	c	28.	a	29.	d	30.	a
31.	b	32.	b	33.	c	34.	d	35.	b

## Hints and Explanations



$$\text{As } V = \frac{n RT}{P}$$

On solving  $n = 8.04$  litre



50 gm

3. First find moles

$$(n) = \frac{PV}{RT}$$

$$= \frac{10^{-4}}{760} \times \frac{1 \times 1}{0.082 \times 298}$$

Number of molecules =  $n \times N_0$

On solving we get

$$= 3.24 \times 10^{15} \text{ molecules}$$

4. Only in case of IV as correct volume must be  $10.5/3.5 = 3$  litre.

5. As  $P \propto T$

$$\text{So } \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

On solving, we get

$$T_2 = 1200 \text{ K}$$

As  $T_2$  is less than melting point of the cylinder so it will neither melt nor burst..

6. As  $P \propto T$

$$\text{So } \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\frac{12}{300} = \frac{14.9}{T_2}$$

On solving, we get

$$T_2 = 372.5 \text{ K}$$

7. (i) First find weight of  $\text{H}_2$

As ratio of H : O in  $\text{H}_2\text{O}$  is 1 : 8 so weight of  $\text{H}_2$  in 2 g water

$$= \frac{2 \times 18}{18} = 2 \text{ g}$$

(ii) Volume of 2 gm  $\text{H}_2$  at NTP

$$= 2 \times 11.2 = 22.4 \text{ lit}$$

(iii) Now apply

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{2 \times 760 \times V_1}{400} = \frac{760 \times 22.4}{273}$$

On solving, we get

$$V_1 = 16.4 \text{ lit}$$

8. Weight of mixture = 10 g

Suppose weight of  $\text{H}_2 = X$  g

So weight of He =  $(10 - X)$  g

$$n(\text{H}_2) = (X/2)$$

$$n(\text{He}) = (10 - X)/4$$

$$PV = n RT$$

$$n = \frac{PV}{RT}$$

$$\left(\frac{X}{2}\right) + \left(\frac{10-X}{4}\right) = \frac{41.5 \times 10^4 \times 0.02}{8.314 \times 320}$$

After solving,  $X = 2.48$  g [mass of  $\text{H}_2$ ]

So weight of He =  $10 - 2.48 = 7.52$  g

9. As  $n = \frac{PV}{RT}$

$$P = 2 \times 10^{-6}/760 \text{ atm}$$

$$T = -160 + 273 = 113 \text{ K}$$

$$R = 0.082$$

$$V = 2/1000 \text{ L or } 2 \times 10^{-3} \text{ L.}$$

On solving, we get

$$n = 5.66 \times 10^{-13} \text{ moles}$$

10. If initial volume is  $V$

Then final volume is  $0.95 V$ .

$$P_1 V_1 = P_2 V_2$$

$$P_2 = \frac{P_1 \times V}{0.95 V} = 1.0526 P_1$$

i.e. 0.0526 is the increase in pressure

$$\text{so } \% = 0.0526 \times 100$$

$$= 5.26 \% \text{ of initial pressure}$$

11. First apply

$$C = \frac{5}{9} (F - 32)$$

$$= 36.88^\circ\text{C} \text{ or } 309.88 \text{ K}$$

$$\text{Now } w = \frac{PV \cdot M}{RT}$$

$$= \frac{168 \times 6 \times 32}{760 \times 0.081 \times 309.88} = 1.67 \text{ g.}$$

$$(12) \text{ As } PV = nRT$$

Since V, T are constant so P  $\propto$  n

$$\frac{P_1}{P_2} = \frac{w_1}{w_2}.$$

On solving, we get

$$w_2 = 12 \text{ kg}$$

So 3 kg gas leaked in one day.

After 3 days total gas leaked will be

$$= 3 \times 3 = 9 \text{ kg}$$

13. Here P, V, R are same

$$\text{So } n_1 T_1 = n_2 T_2$$

$$\text{i.e. } n_1 \times 300 = n_2 \times 500$$

$$n_2 = \frac{3}{5} n_1$$

Number of moles escaped

$$= n_1 - \frac{3}{5} n_1 = \frac{2}{5} n_1$$

$$= 0.4 n_1 = 40 \%$$

14. Height developed due to pressure of gas

$$= 43.7 - 15.6 = 28.1 \text{ cm}$$

$$\text{Now } P = n \times d \times g$$

$$= \frac{28.1 \times 13.6 \times 980}{76 \times 13.6 \times 980} = 0.37 \text{ atm}$$

$$P(\text{gas}) = P(\text{atm}) + 0.37$$

$$= \frac{743}{760} + 0.37$$

$$= 1.347 \text{ atm}$$

$$= 1.347 / 0.987 \text{ bar}$$

$$= 1.36 \text{ bar}$$

15. As  $PV = \frac{w}{M} RT$

$$\text{So } P_X V = \frac{w_X}{M_X} RT [V, T, R \text{ are same}]$$

$$P_Y V = \frac{w_Y}{M_Y} RT$$

$$\frac{P_X}{P_Y} = \frac{w_X}{w_Y} \times \frac{M_Y}{M_X}$$

On solving, we get

$$M_Y = 4 M_X$$

16. As  $d = \frac{PM}{RT}$

$$\text{So } \frac{P_{N_2} \times 28}{RT} = \frac{P_{\text{oxide}} \times M_{\text{oxide}}}{RT}$$

$$M_{\text{oxide}} = \frac{5 \times 28}{2} = 70$$

17. As  $d \propto 1/V$

$$\text{So } \frac{d_T}{d_B} = \frac{V_b}{V_t} = \frac{T_b P_t}{T_t P_b}$$

$$= \frac{303 \times 710}{273 \times 760} = \frac{1.04}{1}$$

$$= 1.04 : 1$$

18. As  $PV = \frac{w}{M} RT$

$$V = \frac{w}{M \times P} \times RT$$

$$= \frac{5}{26} \times \frac{0.082 \times 323}{740} \times 760$$

$$= 5.23 \text{ litre}$$

19. Apply  $V_2 = \frac{(P_1 - f) V_1 T_2}{P_2 T_1}$

$$= \frac{(755 - 23.8) \times 0.55 \times 273}{760 \times 298}$$

$$V_2 = 0.485 \text{ litre.}$$

21. Apply  $P_A = \frac{\% \text{ of A} \times P_{\text{mix}}}{100}$

On solving

$$P_{CO_2} = 152 \text{ mm}$$

$$P_{O_2} = 114 \text{ mm}$$

$$P_{N_2} = 494 \text{ mm}$$

23. Mol. wt. of  $^{235}\text{UF}_6 = 235 + 19 \times 6$

$$= 349$$

$$\text{Mol. wt. of } ^{238}\text{UF}_6 = 238 + 19 \times 6$$

$$= 352$$

## 2.58 ■ Gaseous and Liquid States

So

$$\begin{aligned} r_1/r_2 &= \sqrt{[\text{M. wt. of } {}^{238}\text{UF}_6 / \text{M. wt. of } {}^{235}\text{UF}_6]} \\ &= \sqrt{(352/349)} \\ &= 1.0043/1 \end{aligned}$$

$$\text{so } r_1 : r_2 = 1.0043 : 1$$

26.  $E = \frac{3}{2} RT$  (Kinetic energy of 1 mole gas)

$$\begin{aligned} \Delta &= \frac{3}{2} R(T + 50) - \frac{3}{2} RT \\ &= \frac{3}{2} R \times 50 = \frac{3}{2} \times 8.314 \times 50 \\ &= 623.55 \text{ J} \end{aligned}$$

27.  $V_{\text{r.m.s}} = \frac{\sqrt{3RT}}{\sqrt{M}}$ .

$$\text{So } \sqrt{3RT/2} = \sqrt{[(3R \times 273)/32]}$$

On solving, we get

$$T = 17.06 \text{ K}$$

28.  $v_{\text{av}} = \frac{\sqrt{8RT}}{\sqrt{\pi m}}$

$$\begin{aligned} v_{\text{SO}_2} &= \frac{\sqrt{m_{\text{CH}_4}}}{\sqrt{m_{\text{SO}_2}}} \\ &= \frac{\sqrt{16}}{\sqrt{64}} \\ &= \frac{1}{2} \end{aligned}$$

29.  $b = 4 N \frac{4}{3} \pi r^3$

$$b = 0.0237 \text{ litre mole}^{-1} = 23.7 \text{ ml mole}^{-1};$$

$$N = 6.02 \times 10^{23}$$

30.  $7 = 4 \times 6.02 \times 10^{23} \times (4/3) \times (22/7) \times r^3$

$$r^3 = 23.7 \times 21$$

$$16 \times 6.02 \times 10^{23} \times 22$$

$$r = \frac{(237 \times 21 \times 10^{-24})^1}{(16 \times 6.02 \times 22)^3}$$

$$(16 \times 6.02 \times 22)^{1/3}$$

$$= 1.33 \times 10^{-8} \text{ cm}$$

$$= 2.66 \times 10^{-8} \text{ cm}$$

31. As  $\frac{V_1}{V_2} = \frac{\sqrt{T_1}}{\sqrt{T_2}}$

On solving,

$$V_2 = 0.6 \text{ m/s.}$$

32.  $V_{\text{r.m.s}} = \frac{1}{\sqrt{V a_v}}$ .

$$0.9213$$

$$= 1.086 : 1$$

33. Apply  $P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$

$$= \frac{15 \times 0.082 \times 303}{(12 - 15 \times 0.0171)} - \frac{(15)^2 \times 0.2107}{12}$$

$$= 31.4 \text{ atom.}$$

34. As volume of one molecule = X

$$\text{Volume of } N_0 \text{ molecule} = X N_0$$

$$\text{So } b = 4 N_0 X$$

As 'b' is equal to 4 times of volume of  $N_0$  molecules present in one mole of a gas.

## CHAPTER 3

# Atomic Structure

### Chapter Contents

Bohr model, spectrum of hydrogen atom, quantum numbers, Wave-particle duality, de Broglie hypothesis; Uncertainty principle; Qualitative quantum mechanical picture of hydrogen atom, shapes of s, p and d orbitals; Electronic configurations of elements (up to atomic number 36); Aufbau principle; Pauli's exclusion principle and Hund's rule and Various levels of multiple-choice questions.

### ATOMIC THEORY

The word atom and atomic theory was introduced by John Dalton in 1808 in terms of an atomic model.

#### Main Postulates of Atomic Theory

- Atom is the smallest, undivided fundamental particle. which can neither be created nor destroyed. However, it is interconvertible.
- Atoms undergo chemical combination to form molecules but in whole number ratio, that is, molecule is the smallest identity that exists individually.
- Atoms of same element have same mass, size, property etc., but atoms of different element differ in these properties.

#### Modern View of Atomic Theory

According to J. J. Thomson, an atom is divisible into subatomic particles. Atoms can also combine in non-whole number ratio in non-stoichiometric compounds example.  $\text{Fe}_{0.93}\text{O}$ .

Atoms of same element also differ in properties related to mass even in case of isotopes also.

#### Sub-Atomic Particles or Constituents of Atoms

##### Electrons ( $-e^0$ or $e^-$ )

Electron was discovered by J. J. Thomson during the study of cathode rays (stream of electrons) and named by J. L. Stoney

Location of electron: It is present in extra nuclear region in atom outside the nucleus.

$$\begin{aligned} \text{Mass: Mass of electron} &= \frac{1}{1837} \text{ of H-atom} \\ &= 0.00055 \text{ a.m.u} \\ &= 9.1 \times 10^{-31} \text{ kg} \end{aligned}$$

**Charge:** It is confirmed by Milikan's oil drop experiment and its values are  $1.6 \times 10^{-19} \text{ C}$  or  $-4.8 \times 10^{-10} \text{ e.s.u.}$

### 3.2 ■ Atomic Structure

Thomson gave e/m ratio or specific charge ratio for electron and the value is  $1.76 \times 10^8$  c/gm.

Cathode rays are beam or stream of electrons and e/m ratio for cathode rays is constant and independent of nature of gas in discharge tube and nature of cathode or electrodes of tube that is, electron is an universal fundamental particle.

■ Mass of one mole of electron is 0.55 mg.

■ Mass of moving  $e^- = \frac{m_{\text{rest}}}{\sqrt{1 - (V/C)^2}}$ .

Here V = Velocity of electron

C = Velocity of light

- Electron can leave its orbit for maximum  $10^{-8}$  sec.
- Particle nature of electron is confirmed by scintillation effect on ZnS screen.
- Photoelectric effect, emission of  $\beta$ -particle, thermal emission or heating of metal filament confirm fundamental particle nature of electron.
- Density of electron is  $2.17 \times 10^{17}$  gm/c.c.

#### REMEMBER

e/m ratio or specific charge ratio or Thomson ratio order:

$${}_{-1}e^0 > {}_1p^1 > {}_2\alpha^4 > {}_0n^1$$

zero as it is  
charge less particle

#### Proton ( ${}_1H$ or p)

Proton was discovered by Goldstein during the study of anode rays or canal rays or +ve rays which originate in the region between cathode and anode in discharge tube. Proton was named by Rutherford.

For anode rays, e/m ratio depends upon nature of gas taken in a discharge tube. It is maximum for hydrogen gas.

Charge on proton is  $+ 1.6 \times 10^{-19}$  or  $+ 4.8 \times 10^{-10}$  e.s.u

Mass of proton is that of H-atom that is,  $1.673 \times 10^{-27}$  kg or 1.0072 a.m.u.

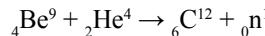
e/m ratio is  $9.5 \times 10^4$  c/gm

1 a.m.u. = 1/12 mass of C-atom

1 a.m.u =  $1.66 \times 10^{-27}$  kg = 931.5 MeV

#### Neutron ( ${}_0n$ )

Neutron was discovered by Chadwick as follows



Neutron was discovered late because it is chargeless.

- It is heavier than electron and proton.
- Isolated neutron is unstable and disintegrates as follows:  
$${}_0n^1 \rightarrow {}_{-1}e^0 + {}_1p^1 + \nu$$
- It is stable inside the nucleus but unstable outside the nucleus.
- It is the best projectile as it is chargeless.
- H-atom has no neutron.

Mass of neutron is  $1.674 \times 10^{-27}$  kg or 1.0086 a.m.u

Density of neutron is  $1.5 \times 10^{14}$  g/c.c.

**Atomic Number (Z)** Moseley postulated the frequency of the X-rays was related to the charge present on the nucleus of the atom of the element used as anticathode and found that

$$\sqrt{\nu} = a(Z - b)$$

Here  $\nu$  is the frequency, Z is the nuclear charge and a and b are constants.

a = probability constant

b = a constant having same values for all lines of X-ray spectrum.

The number of unit positive charges carried by the nucleus of an atom is called the atomic number of the element that is,

$$Z = p = e \text{ (from atoms)}$$

$$Z = p \text{ (for ions)}$$

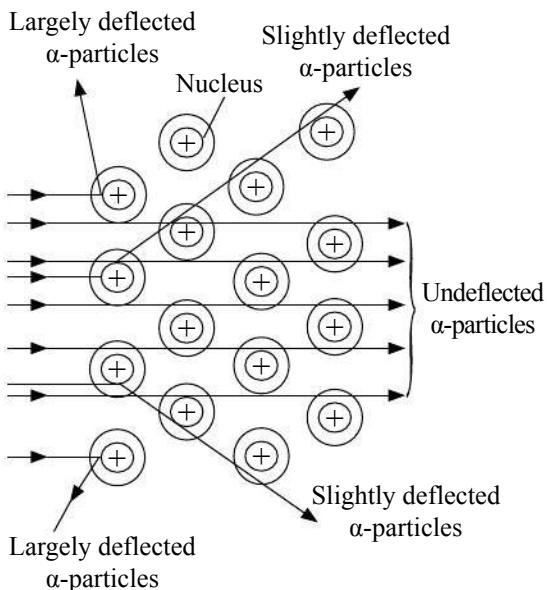
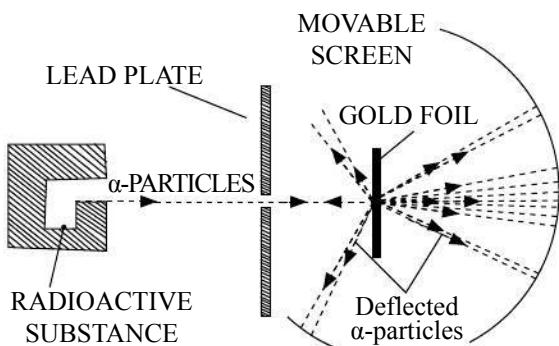
#### Facts about Atomic number

- It is always a whole number, and a permanent value for each element.
- It is serial number of elements in periodic table that is, determines their exact position.
- Periodic properties are related to the atomic number of elements.

**Mass number (A):** Mass number is nearly equals to atomic weight and mathmetically, it is the sum of proton + neutron.

$$A = p + n = Z + n$$

## RUTHERFORD'S ATOMIC MODEL



During  $\alpha$ -particle or helium nuclei bombardment experiment on  $10^{-4}$  mm thick gold foil, Rutherford observed that:

- (i) Most part of the atom is empty as most of the  $\alpha$ -particles passed straight through the foil without any deflection.
- (ii) Electrons occupy position in this empty space (extra nuclear region).

(iii) Centrally located solid compact small part having all positive charge and nearly the whole mass is called nucleus. (as few one out of 20,000  $\alpha$ -particles get defected  $>$ up to  $90^\circ$  and maximum  $180^\circ$ )

(iv) The size or radius of nucleus can be calculated by this relation and Radius of atom is  $10^{-10}$  m. or  $10^{-8}$  cm.

$$r = 1.3 \times 10^{-13} \times A^{1/3} \text{ cm}$$

Here  $A$ =Mass number

$r$  = radius of nucleus

The density of nucleus (Assumed as spherical) can be find out as

$$d = \frac{M}{V} = \frac{A}{N_A} \times \frac{1}{4/3 \pi r^3} = 1.8 \times 10^4 \text{ g/cm}^3$$

Radius of nucleus =  $10^{-15}$  m. or  $10^{-13}$  cm.

Atomic radius  $>$  nucleus radius by  $10^5$  times.

Density of nucleus is  $10^{17}$  kg/m<sup>3</sup> or  $10^{14}$  gm/cm<sup>3</sup> and volume of nucleus is  $10^{-39}$  cm<sup>3</sup>.

### REMEMBER

- Scattering of  $\alpha$ -particles  $\propto \frac{1}{\sin^4(\theta/2)}$ .

- (v) Centrifugal force develops between electrons and nucleus so electron revolve around the nucleus as stars move around the sun. (that is, planetary or solar model).

### Merits

- (i) Explains discovery of nucleus.
- (ii) Explains Circulatory rotation of electron around the nucleus.

### Demerits

- (i) It cannot explain stability of atom.
- (ii) It cannot explain the number and velocity of electrons.
- (iii) According to him, atomic spectrum is continuous and non-linear but infact it may be linear and discontinuous.

## Quantum Theory

It was introduced by Max Planck and then extended by Einstein.

### 3.4 ■ Atomic Structure

Quantum Theory states that hot vibrating body does not emit or absorb energy continuously but emits or absorbs discontinuously in the form of small energy packets or bundles known as quanta and photon in case of light energy.

The energy of radiation (E) is directly proportional to frequency of radiation ( $\nu$ ).

$$E \propto \nu$$
$$E = h \nu = h \frac{c}{\lambda} = hc\bar{\nu}$$

Here  $h$  is Planck's constant and its values is  $6.6253 \times 10^{-34}$  Js or  $\text{Kg m}^2 \text{s}^{-1}$ .

$\lambda$  = Wavelength,  $\bar{\nu}$  = wave number

Absorption or emission in the form of multiples of quantum is known as quantization of energy that is,

$$E = n h \nu$$

A hollow sphere coated inside with platinum black and having a small hole in its wall acts as a black body. It is a perfect absorber and perfect emitter of radiant energy.

At a given temperature the intensity of radiation increases with wavelength, approaching towards maximum and then starts decreasing.

As Planck's quantum theory can explain only the black body radiations so Einstein extended quantum theory to all types of electromagnetic radiations.

### Illustrations

- Calculate the frequency of the light ray emitted when an electron drops from a higher to a lower energy level of an atom, the difference between the energies of which is  $35.64 \times 10^{-13}$  erg.

(Plancks's constant;  $h = 6.624 \times 10^{-27}$  erg s)

**Solution**  $E = h \nu$

$$\nu = \frac{E}{h} = \frac{35.64 \times 10^{-13}}{6.624 \times 10^{-27}}$$
$$= 5.38 \times 10^{14} \text{ s}^{-1}$$

- 3  $\times 10^{18}$  photons of a certain light radiation produce 1.5 J of energy. Find out the wave length of this radiation ( $h = 6.626 \times 10^{-34}$  JS).

**Solution**  $E = h \nu$  (for one photon)

$E = N h \nu$  (for  $N$  photons)

$$E = \frac{N h c}{\lambda}$$

$$\lambda = \frac{N h c}{E} = \frac{3 \times 10^{18} \times 6.62 \times 10^{-34} \times 3 \times 10^8}{1.5}$$

$$= 39.75 \times 10^{-8} \text{ m} = 3975 \text{ \AA}.$$

- How many mole of photons would contain sufficient energy to raise the temperature of 220 g of water from 25°C to 100°C? Specific heat of water is  $4.184 \text{ J g}^{-1} \text{ K}^{-1}$  and frequency of light radiation used is  $2.40 \times 10^9$  Hz.

**Solution** The energy need to change the temperature from 25°C to 100°C is given as follows:

$$E = m s \Theta$$

Here  $m$  = Mass

$s$  = Specific heat

$\Theta$  = Temperature change

$$E = 220 \times 4.184 \times 75 \text{ Joule}$$

$$E = 69036 \text{ Joule}$$

For a radiation of  $2.4 \times 10^9$  Hz

The energy is given as follows:

$$E = n h \nu$$

$$= 2 \times 6.626 \times 10^{-34} \times 2.4 \times 10^9$$

So,

$$n \times 15.9024 \times 10^{-25} = 69036$$

$$n = \frac{69036}{15.9024} \times 10^{25}$$

$$n = 4.34123 \times 10^{28}$$

Hence moles of photons =  $\frac{n}{N_0}$ .

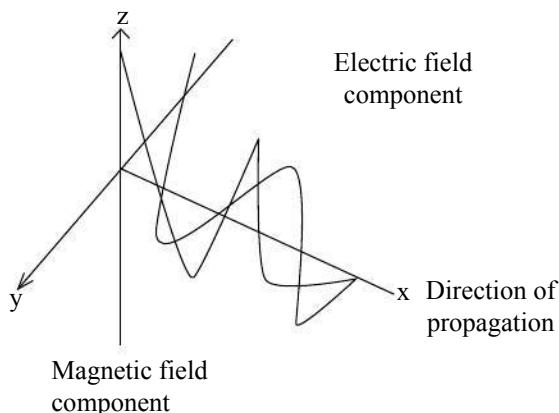
$$= \frac{4.34123 \times 10^{28}}{6.02 \times 10^{23}} = 7.211 \times 10^4 \text{ moles}$$

### Electronic Structure of Atoms

#### Wave Theory

It is described in brief as follows:

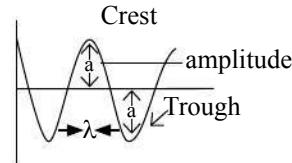
- All radiant energy propagates in terms of waves.
- Radiant energy is in the form of electromagnetic waves
- The radiations are associated with electric and magnetic field perpendicular to one another.
- In the propagation of an electromagnetic radiation there is only propagation of wave but not that of the medium.



The electric and magnetic field components of an electromagnetic wave. These components have the same wavelength, frequency, speed and amplitude, but they vibrate in two mutually perpendicular planes.

### Wavelength

It is the distance between any two successive crests or two successive troughs of waves. It is denoted by  $\lambda$  and it is measured in Å (Angstroms) or nm (nanometers) etc.



### Frequency

It is the number of waves passing at a given point per second. It is denoted by  $v$  or  $f$ . The units of frequency are Hertz or cycles sec<sup>-1</sup>.

### Velocity of Light

It is the distance traveled by one wave in one second.

$$\text{Velocity of light} = \text{frequency} \times \text{wave length}$$

$$C = v\lambda$$

$$\lambda \propto 1/v$$

Light or all electromagnetic radiations travels in vacuum or air with same velocity.

### Wave Number

It is the number of waves spread in one cm and it is denoted by  $v^-$ .

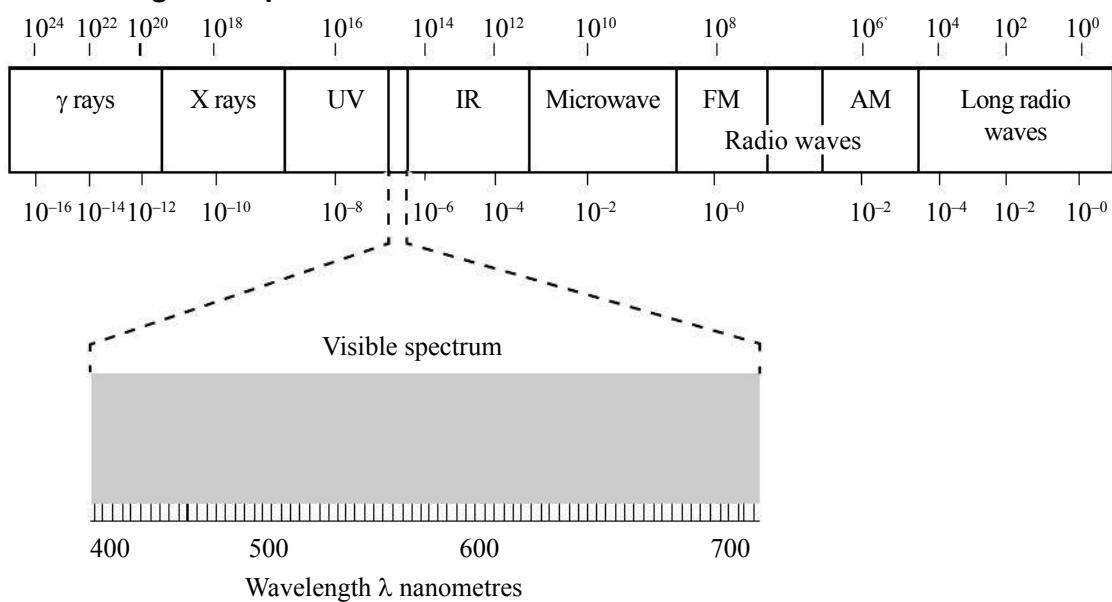
It is the reciprocal of wavelength.

$$v^- = \frac{1}{\lambda}, \text{ as } v^- = \frac{C}{\lambda}$$

$$\text{So } v^- = C \nu$$

Its units are cm<sup>-1</sup> or m<sup>-1</sup>.

### Electromagnetic Spectrum



The spectrum of electromagnetic radiation. The visible region is only a small part of the entire spectrum  
 (a) Overall spectrum (b) Visible region.

## Corpuscular Theory of Light

It was first introduced by Newton. According to this theory, light is propagated in the form of small invisible particles.

## Photoelectric Effect

It was introduced by P. Lenard and explained by Einstein. It is the emission of electrons from a metal surface on exposing it to radiation of suitable frequency or wavelength. It is readily shown by alkali metals like K and Cs having very low ionization energy.

When a photon strikes the metal, its energy is absorbed by the electrons and emission of electrons takes place.

A part of the energy of photon is used to escape the electron from the attractive forces and the remaining energy is used in increasing the kinetic energy of electron.

$$\text{K.E.} (\frac{1}{2}mv^2) = E - \Phi$$

Here E = energy of radiation.

$\Phi$  = work function (minimum energy needed for electron emission).

$$\text{K.E.} = hv - hv_0$$

$v_0$  = threshold frequency (minimum frequency of light radiation needed for electron emission).

If  $v > v_0$

K.E. is +ve electron is emitted

If  $v = v_0$

K.E. = 0 electron is not emitted (remains on surface)

If  $v < v_0$

K.E. is -ve no emission of electrons.

Photoelectric effect  $\propto$  Frequency of light radiation

Kinetic energy of electrons does not depend upon intensity of light, however, number of ejected electrons depend upon intensity of light.

## Stopping Potential

The minimum potential applied by which velocity of ejected photoelectron becomes zero. This potential is called stopping potential.

$$\frac{1}{2}mv^2 = eVs$$

$$V_s = \frac{mv^2}{2e}$$

Here

$V_s$  = Stopping potential

m = Mass of electron

v = Velocity of ejected electron

e = charge of electron

## Einstein's Photoelectric Equation

$$E = W + \text{K.E.}$$

$$hv = hv_0 + \frac{1}{2}mv^2$$

$$hv = hv_0 + eV_s$$

Here v = Frequency of incident radiation.

## Work Function

The minimum energy required for the photoelectric effect is called work function.

$$W = hv_0$$

$$W = \frac{hc}{\lambda_0}$$

Here

c = Velocity of light

$\lambda_0$  = Threshold wavelength

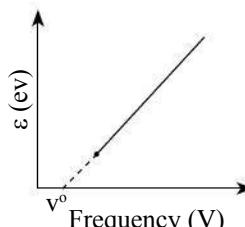


Fig. 3A

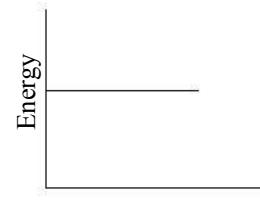


Fig. 3B

## Illustrations

4. Determine the wave length of a photon of electromagnetic radiation having energy  $2.99 \times 10^{12} \text{ erg mol}^{-1}$  ( $h = 6.625 \times 10^{-34}$ ).

**Solution**  $\lambda = \frac{N hc}{E}$

$$= \frac{6.023 \times 10^{23} \times 6.625 \times 10^{-34} \times 3 \times 10^8}{2.99 \times 10^{12}}$$

$$= 4000 \text{ Å.}$$

5. When a certain metal was irradiated with a light of frequency  $1.5 \times 10^{16} \text{ Hz}$ , the photoelectrons

emitted had twice the kinetic energy as did photoelectrons emitted when the same metal was irradiated with light of frequency  $1.0 \times 10^{16}$  Hz. Find  $v_0$  (threshold frequency) for the metal.

**Solution**  $E_1 = h(v_1 - v_0)$  .... (i)

$$E_2 = h(v_2 - v_0) = E_{1/2} \quad \dots \dots \text{(ii)}$$

On diving equation (ii) by (i), we get

$$\frac{v_2 - v_0}{v_1 - v_0} = \frac{1}{2}$$

$$\frac{1.0 \times 10^{16} - v_0}{1.5 \times 10^{16} - v_0} = \frac{1}{2}$$

$$2.0 \times 10^{16} - 2v_0 = 1.5 \times 10^6 - v_0$$

On solving, we get

$$v_0 = 5 \times 10^{15} \text{ Hz}$$

6. Calculate the kinetic energy of the electron emitted by an atom by 400 nm light when its threshold wavelength is 600 nm ( $n = 6.63 \times 10^{-34}$  Js and  $c = 3 \times 10^8 \text{ ms}^{-1}$ ).

**Solution** As  $\text{K.E.} = h(v - v_0) = hc(1/\lambda - 1/\lambda_0)$

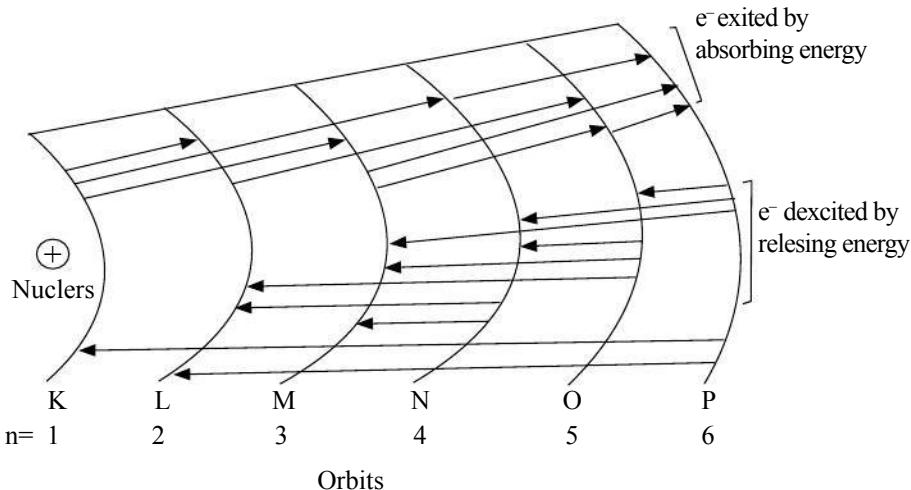
$$\text{K.E.} = 6.626 \times 10^{-34} \times 3 \times 10^8 \times \left( \frac{1}{400} - \frac{1}{600} \right) \times 10^9$$

$$\text{K.E.} = \frac{6.626 \times 3 \times 10^{-17}}{1200} = \frac{6.626 \times 10^{-19}}{4} \text{ J}$$

$$\text{K.E.} = 1.656 \times 10^{-19} \text{ J}$$

## BOHR'S ATOMIC MODEL

Bohr introduced Circular orbit concept based on (Linear hybrid combination of classical and early quantum physics) and Planck's quantum theory and it's main postulates are as follows:



- Around the nucleus there are circular regions or spherical surfaces which are called orbits or shells. Each orbit has a fix amount of energy so it is called energy level.

K	L	M	N	O .....
$n = 1$	2	3	4	5 .....

Energy and distance from nucleus increase

- Angular momentum ( $mvr$ ) of an electron moving in any orbit is quantized and given as

$$Mvr = n \frac{h}{2\pi} \Rightarrow nh$$

here  $h$  is plank's constant.

Here  $n$  is an integer with whole number values  $1, 2, 3, \dots$  and known as Principal Quantum number

$n \rightarrow$	1	2	3	4	5
$mvr \rightarrow$	$\frac{h}{2\pi}$	$\frac{h}{\pi}$	$\frac{3h}{2\pi}$	$\frac{2h}{\pi}$	$\frac{5h}{2\pi}$ .....

- An electron revolves round the nucleus in a particular orbit having definite energy without any

### 3.8 ■ Atomic Structure

change of energy or any radiation of energy that is why these orbits are called stationary states are stable or non-radiating orbits. The force of attraction between the nucleus and the electron is equal to centrifugal force of the revolving electron. When electron changes its orbit energy change occurs in quanta which is given as follows

$$\Delta E = E_2 - E_1 = h\nu \text{ or } = \frac{hc}{\lambda} \text{ quanta}$$

Quanta is a small bundle of any type of energy, while Photon is a small mass less bundle of light energy and not a material body.

- In excited state: electron jumps from lower to higher orbit or energy level by absorbing energy in quanta. While in de-excited, electron jumps from higher to lower energy level by releasing energy in quanta.

#### Advantages

- It can explain linear nature of spectrum of hydrogenic species (that is, with one  $e^-$ )

Example, H,  $\text{He}^+$ ,  $\text{Li}^{+2}$  etc.

#### Bohr's Theory for Hydrogen Atom

Let the electron of mass be 'm' is moving around the nucleus with velocity 'v' and radius of circular path 'r'. When electron moves around the nucleus, it experiences coulomb force and centrifugal force. Both these forces balance to each other.

$$\text{Coulomb force } (F_1) = \text{Centrifugal force } (F_2)$$

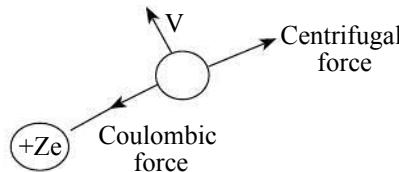
$$\frac{K(Ze)e}{r^2} = \frac{mv^2}{r}$$

$$\frac{KZe^2}{r} = mv^2 \quad \dots\dots\dots(1)$$

$$v^2 = \frac{KZe^2}{rm}$$

Here

$$K = \frac{1}{4\pi\epsilon_0}$$



#### ■ In the calculation of radius of nth orbit (rn):

$$\text{As } mvr = \frac{nh}{2\pi} \quad \dots\dots\dots(2)$$

$$\text{So } v = \frac{nh}{2\pi rm}$$

On putting the value of v in equation number 1 we get the value of radius (r) as follows

$$r_n = \frac{n^2 h^2}{K 4\pi^2 Z e^2 m}$$

On putting the values of h, e, m, n and Z for H-atom in 1st orbit radius is given as

$$r_1 = 0.53 \text{ Å}$$

(The value of  $\frac{h^2}{K 4\pi^2 e^2 m}$  is found to be 0.53 Å)

so for nth orbit radius ( $r_n$ )

$$r_n = 0.53 \times \frac{n^2}{Z} \text{ Å}$$

As  $r \propto 1/n \propto Z$  so radius ratio in two different orbits for two different species is given as

$$\frac{r_{n1}}{r_{n2}} = \frac{n_1^2}{n_2^2} \times \frac{Z_2}{Z_1}$$

#### ■ In the calculation of velocity of electron in nth orbit (Vn):

Similarly from eq (1) and (2) we get

$$V_n = \frac{2\pi^2 K Z e^2}{nh}$$

As for an electron in first orbit of Hydrogen atom velocity is given as

$V_1 = 2.18 \times 10^6 \text{ m/s}$  (The value of  $\frac{2\pi^2 K e^2}{h}$  is found to be  $2.18 \times 10^6 \text{ m/s}$ )

$$\text{so } V_n = 2.18 \times 10^6 \times \frac{Z}{n} \text{ m/sec}$$

As

$$V \propto Z \propto \frac{1}{n}$$

So the ratio of velocity in two different orbit for two different species can be given as

$$\frac{V_{n1}}{V_{n2}} = \frac{Z_1}{Z_2} \times \frac{n_2}{n_1}$$

#### REMEMBER

$V_1$  for H-Atom =  $V_2$  of  $\text{He}^+$  =  $V_3$  for  $\text{Li}^{+2}$  =  $2.18 \times 10^6 \text{ m/s}$  (Bohr's velocity)

■ In the calculation of energy of electron in nth orbit ( $E_n$ ):

The total Energy (Et) for an electron in any orbit is given as:

$$\text{as } E_T = E_{\text{KE}} + E_{\text{PE}}$$

$$= \frac{1}{2} MV^2 + E_{\text{PE}} \quad [\text{as } MV^2 = \frac{KZe^2}{r}]$$

$$E_T = \frac{1}{2} \frac{KZe^2}{r} + \frac{(-KZe^2)}{r} \quad [\text{as } P_E = -\frac{KZe^2}{r}]$$

$$E_T = \frac{-1}{2} \frac{KZe^2}{r}$$

It means

$$E_{\text{KE}} = -E_T$$

$$2E_{\text{KE}} + \text{P.E} = \text{Zero}$$

$$E_n = \frac{-KZe^2}{2r_n}$$

On putting the value of  $r_n$  here we got

$$E_n = \frac{-2K^2 \pi^2 Z^2 m e^4}{n^2 h^2}$$

$$\text{If the value of } \frac{2K^2 \pi^2 M e^4}{h^2}$$

$$= 2.18 \times 10^{-18} \text{ J/atom}$$

$$= 13.6 \text{ e.v /atom}$$

$$E_n = -2.18 \times 10^{-18} \times \frac{Z^2}{n^2} \quad \text{J /atom}$$

$$= -13.6 \times \frac{Z^2}{n^2} \quad \text{e.v/atom}$$

$$= -313.6 \times \frac{Z^2}{n^2} \quad \text{K.cal./mole}$$

$$\text{As } E_n \propto Z^2 \propto \frac{1}{n^2}$$

$$\text{So } \frac{E_{n_1}}{E_{n_2}} = \frac{Z_{n_1}^2}{Z_{n_2}^2} \times \frac{n_{n_2}^2}{n_{n_1}^2}$$

### REMEMBER

Bohr energy =  $-13.6 \text{ eV/atom}$  ( It is also  $E_1$  for H-Atom,  $E_2$  for  $\text{He}^+$  and  $E_3$  for  $\text{Li}^{+2}$

$$\text{■ Number of revolutions per sec.} = \frac{Vn}{2\pi r_n}$$

$$= \frac{Z^2}{n^3} \times 6.666 \times 10^{15}$$

$$\text{■ Time Period of revolution in nth orbit (Tn)}$$

$$= \frac{2\pi r_n}{Vn} = \frac{n^3}{Z^2} \times 1.5 \times 10^{-16} \text{ sec}$$

### Illustrations

7. Calculate the velocity ( $\text{cm s}^{-1}$ ) of an electron placed in the third orbit of the hydrogen atom. Also calculate the number of revolutions per second that this electrons makes around the nucleus.

**Solution** Velocity of an electron in the nth orbit

$$V_n = \frac{2\pi e^2}{nh}$$

$$= \frac{2 \times 3.14 \times (4.8 \times 10^{-10} \text{ esu})^2}{3 \times 6.626 \times 10^{-34} \text{ erg s}}$$

$$= 7.27 \times 10^7 \text{ cm s}^{-1}$$

Revolution per second

$$= \frac{V_n}{2\pi r_n} = \frac{2\pi e^2}{nh} \times \frac{1}{2\pi} \times \frac{4\pi^2 Z m e^2}{n^2 h^2}$$

$$= \frac{4\pi^2 Z m e^4}{n^3 h^3}$$

$$= \frac{4 \times (3.14)^2 \times 1 \times 9.10 \times 10^{-28} \times (4.8 \times 10^{-10})^4}{(3)^3 \times (6.626 \times 10^{-34})^3}$$

$$= 2.42 \times 10^{14}$$

8. An electron is in one of the excited state in H-atom, whose radius is  $2.115 \text{ \AA}$ . Find the wavelength of a photon which will remove this electron H-atom.  $R_H = 1.097 \times 10^7 \text{ m}^{-1}$ .

**Solution**  $r_n = 0.529 \times \frac{n^2}{Z} \text{ \AA}$

$$2.116 = 0.529 \times \frac{n^2}{1} \text{ \AA}$$

$$\text{On solving } n = 2$$

To find  $\lambda$ , use this relation

$$\frac{1}{\lambda} = R_H Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\frac{1}{\lambda} = 109678 \left( \frac{1}{2^2} - \frac{1}{\infty^2} \right)$$

On solving

$$\begin{aligned} \lambda &= 3.646 \times 10^{-5} \text{ cm} \\ &= 3.646 \times 10^{-7} \text{ m} \\ &= 3646 \text{ \AA} \end{aligned}$$

### 3.10 ■ Atomic Structure

#### Ionization Energy and Excitation Energy

Excitation potential for  $n_1 \rightarrow n_2$

$$= \frac{E_{n_2} - E_{n_1}}{\text{Electronic charge}}$$

Ionization potential for  $n_1 \rightarrow \infty$

$$= \frac{E_{n_1}}{\text{Electronic charge}}$$

The energy required to remove an electron from the ground state to form cation, that is, to take the electron to infinity, is known as ionisation energy (I.E. or I).

$$\text{I.E.} = E_{\infty} - E_{\text{Ground}}$$

$$\text{I.E.} = 0 - E_1 (\text{H}) = 13.6 \text{ eV atom}^{-1}$$

$$= 2.17 \times 10^{-18} \text{ J atom}^{-1}$$

$$\text{I.E.} = \frac{Z^2}{n^2} \times 13.6 \text{ eV}$$

$$\frac{I_1}{I_2} = \frac{Z_1^2}{n_1^2} \times \frac{n_2^2}{Z_2^2}$$

$$(I.E.)_Z = \frac{(I.E.)_H \times Z^2}{n^2}$$

If an electron is already present in the excited state, the energy required to remove that electron is called separation energy.

$$E_{\text{Separation}} = E_{\infty} - E_{\text{Excited}}$$

$$= 13.6 \times \frac{Z^2}{n^2} \text{ e.v}$$

#### Illustrations

9. The ionization energy of hydrogen atom is 13.6 eV. What will be the ionization energy of  $\text{He}^+$  and  $\text{Li}^{2+}$  ions.

**Solution** Ionization energy of hydrogen ( $\text{H} \rightarrow \text{H}^+ + \text{e}^-$ ) is 13.6 eV.

As the ionization energy of hydrogen like ion may be given as  $Z^2$  (I.E.), so ionization energy of  $\text{He}^+$  is  $2^2 \times 13.6 = 54.4$  eV and  $\text{Li}^{2+}$  is  $3^2 \times 13.6 = 122.4$  eV.

10. The energy of the electron in the second and third Bohr orbits of the hydrogen atom is  $-5.42 \times 10^{-12}$  erg and  $-2.41 \times 10^{-12}$  erg respectively. Calculate the wavelength of the emitted radiation when the electron drops from third to second orbit.

**Solution**  $E_3 - E_2 = h\nu$

$$\nu = \frac{E_3 - E_2}{h}$$

$$= \frac{(-2.41 \times 10^{-12}) - (-5.42 \times 10^{-12})}{6.626 \times 10^{-34}}$$

$$= 0.4543 \times 10^{15} \text{ s}^{-1}$$

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^8}{0.4543 \times 10^{15}} = 6.6036 \times 10^{-7}$$

$$\text{m} = 6603.6 \text{ Å}$$

11. The ionization energy of  $\text{He}^+$  is  $19.6 \times 10^{-18} \text{ J atom}^{-1}$ . Calculate the energy of the first stationary state of  $\text{Li}^{2+}$ .

**Solution** Energy of the first orbit of  $\text{Li}^{2+}$

$$(E_{\text{He}^+})_1 = -Z^2_{\text{He}} \text{ (constant)}$$

$$(E_{\text{Li}^{2+}})_1 = -Z^2_{\text{Li}} \text{ (constant)}$$

$$(E_{\text{Li}^+})_1 = \frac{Z^2_{\text{Li}}}{Z^2_{\text{He}}} (E_{\text{He}^+})_1$$

$$= \frac{3^2}{2^2} \times 19.6 \times 10^{-18} \text{ J atom}^{-1}$$

$$= 44.1 \times 10^{-18} \text{ J atom}^{-1}$$

#### Drawbacks of Bohr's Theory

- It is not applicable for species having more than one electron like Li, He etc.
- It cannot explain fine spectrum of H,  $\text{Li}^{++}$  also.
- It gives no explanation of Zeeman and Stark effects.

#### Zeeman Effect

It is the splitting of main spectrum line into several lines in a strong magnetic field.

#### Stark Effect

It is the splitting of main spectrum line into several lines in a strong electric field

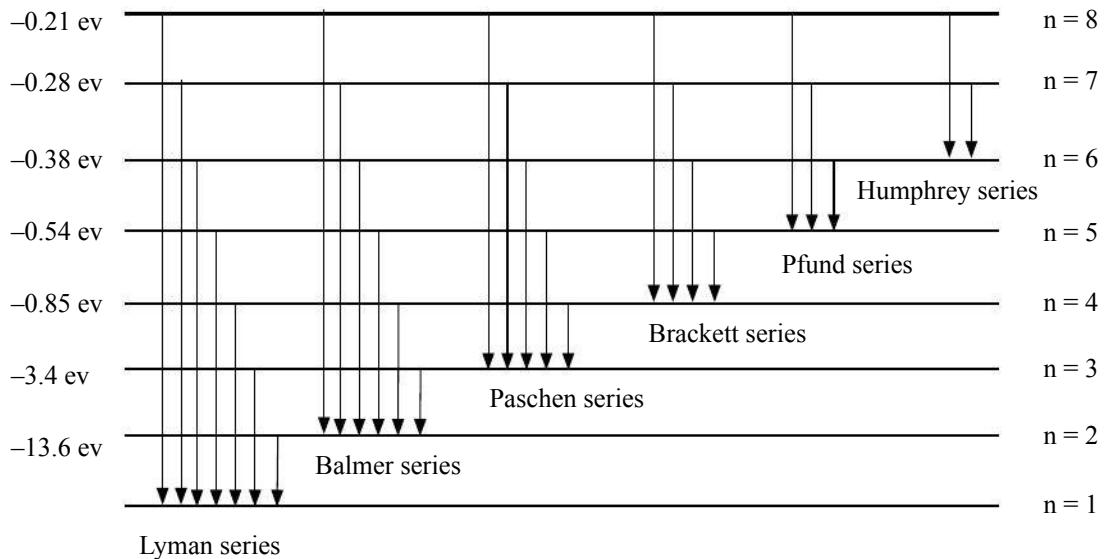
- It can not explain chemical bonding or why atoms combined together to form molecules.
- It can explain only particle nature that is, no explanation of wave nature. (that is, against de Broglie, Heisenberg's, Plank's theory etc.)

#### SPECTRUM OF HYDROGEN ATOM

The atoms of hydrogen in gas discharge tube emit radiations whose spectrum shows line characteristics (line spectra) and lies in the infra red, visible and ultraviolet region of the electromagnetic spectrum.

The most striking feature in hydrogen spectrum is that only some sharply defined discrete wavelength are observed in the emitted radiations.

Example, when a light of wavelength 6563 Å is observed and then light of wavelength 4861 Å is observed. Hydrogen atom do not emit any radiation between 6563 and 4861 Å.

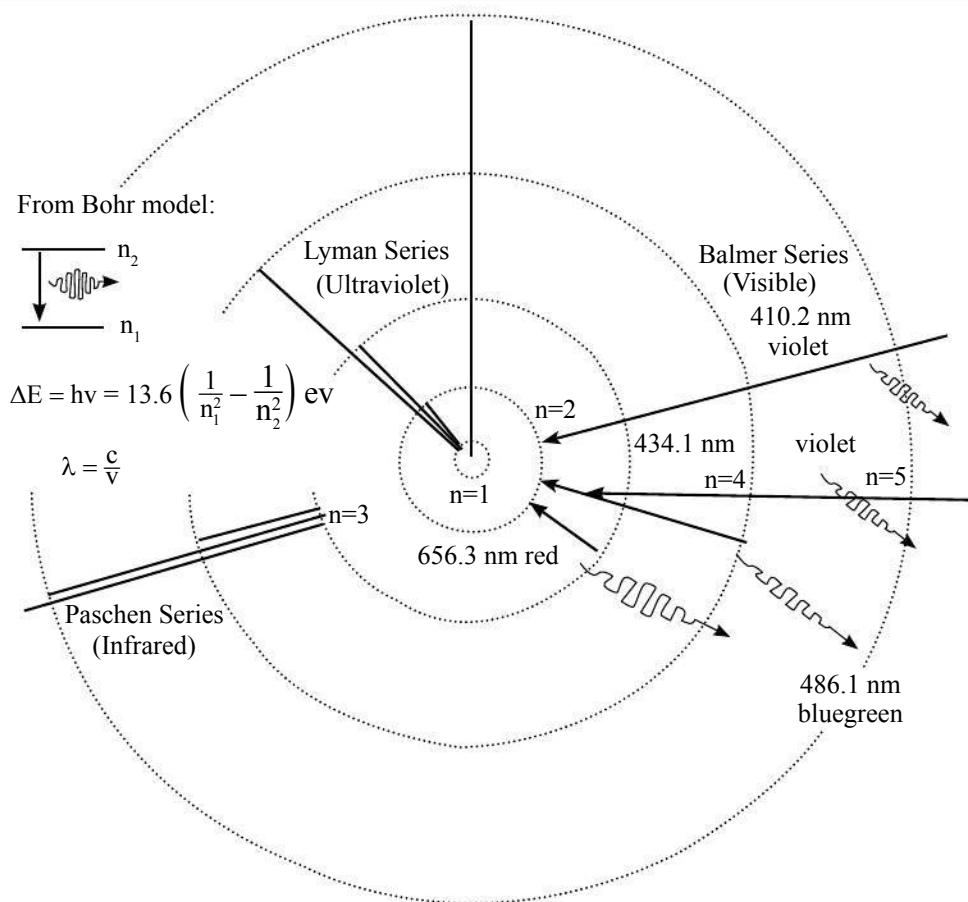


### (ENERGY LEVEL DIAGRAM OF HYDROGEN SPECTRUM)

Hydrogen spectrum has following type of lines:-

	n <sub>1</sub>	n <sub>2</sub>	spectrum region	
Lyman	1	2,3,∞	U.V	912–1216
Balmer	2	3,4,∞	Visible	3646–6561
Paschen	3	4,5,∞	Near Infra Red	8201–18746 Å°
Bracket	4	5,6,∞	FAR I.R	14580–40501 Å°
Pfund	5	6,7,∞	FAR I.R	22782–74588 Å°
Humphries	6	7,8,∞	FAR I.R	32822–123751 Å°

Electronic transition	Name of line	Wave number	Wavelength	Colour
n <sub>2</sub> = 3 → n <sub>1</sub> = 2 (M)                   (L)	H <sub>α</sub> (First line)	– v = 5R/36	λ = 6563 Å	Red
n <sub>2</sub> = 4 → n <sub>1</sub> = 2 (N)                   (L)	H <sub>β</sub> (Second line)	– v = 3R/16	λ = 4861 Å	Blue
n <sub>2</sub> = 5 → n <sub>1</sub> = 2 (O)                   (L)	H <sub>γ</sub> (Third line)	– v = 21R/100	λ = 4340 Å	Indigo
n <sub>2</sub> = 6 → n <sub>1</sub> = 2 (P)                   (L)	H <sub>δ</sub> (Fourth line)	– v = 8R/36	λ = 4102 Å	Violet



### Balmer Series in the Hydrogen Spectrum

Red	Blue-green	Indigo	Violet
6563	4861	4340	4102

Balmer series contains four important lines whose wavelengths are 6563 Å, 4862 Å, 4341 Å and 4102 Å. These are called  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$  and  $H_\delta$  lines.

### To find Spectrum lines

Maximum number of lines obtained when an electron jumps from  $n$ th level to ground level is given as

$$\text{Number of spectrum lines} = \frac{n(n-1)}{2}$$

Example. When  $n$  is 5, number. of lines =  $\frac{5(5-1)}{2} = 10$  lines

Maximum number of lines obtained when an electron returns from  $n_2$  to  $n_1$  is given as

$$\text{No. of lines} = \frac{(n_2-n_1)(n_2-n_1+1)}{2}$$

E.g., when  $n_2=5$   $n_1=2$

$$\begin{aligned} \text{lines} &= \frac{(5-2)(5-2+1)}{2} \\ &= \frac{3(4)}{2} = 6 \end{aligned}$$

### Derivation of Rydberg Equation

$$\Delta E = \frac{hc}{\lambda} = \frac{2\pi^2 Me^4 Z^2}{h^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{2\pi^2 Me^4 Z^2}{h^3 C} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\text{If } R_H = \frac{2\pi^2 Me^4 Z^2}{h^3 C}$$

$$\bar{\nu} = \frac{1}{\lambda} = R_H Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$\bar{\nu}$  = wave number,  $\lambda$  = wavelength

$n_1$  = lower orbit,  $n_2$  = higher orbit

$R_H$  = Rydberg constant and its values are  $109678 \text{ cm}^{-1}$  or  $1.1 \times 10^7 \text{ m}$ .

### REMEMBER

- For longest wavelength or shortest energy or first line of a series,  $n_2$  must be nearest (next value) to  $n_1$ . While for shortest wavelength or highest energy,  $n_2$  must be infinite.
- The intensities of spectral line in a series decrease with the increase in the value of  $n_2$ .

### Illustrations

12. Find out the wavelength of radiations emitted produced in a line in Lyman series, when an electron falls from fourth stationary state in hydrogen atom. ( $R_H = 1.1 \times 10^7 \text{ m}^{-1}$ )

**Solution**  $\frac{1}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ .

For Lyman series  $n_1 = 1$ ,  $n_2 = 4$

$$\begin{aligned}\frac{1}{\lambda} &= 1.1 \times 10^7 \left( \frac{1}{1^2} - \frac{1}{4^2} \right) \\ &= 0.9696 \times 10^{-7} \text{ m}.\end{aligned}$$

13. Find out the wavelength of  $H_\alpha$  line of hydrogen spectrum in the Balmer series. ( $R_H = 109676 \text{ cm}^{-1}$ )

**Solution**  $\frac{1}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ .

For Balmer series  $n_1 = 2$  and for H,

$n_2 = 3$  (first line of Balmer series)

$$\begin{aligned}\frac{1}{\lambda} &= 109676 \left( \frac{1}{2^2} - \frac{1}{3^2} \right) \\ &= 109676 (1/4 - 1/9)\end{aligned}$$

$$\begin{aligned}&= 109676 \times \frac{5}{36} \text{ cm}^{-1} \\ &= \frac{36}{5 \times 109676} \text{ cm} \\ &= 65.65 \times 10^{-6} \text{ cm} \\ &= 6564 \text{ Å}.\end{aligned}$$

14. Calculate the wavelength and energy of the radiation emitted for the electronic transition from infinity ( $\infty$ ) to stationary state first of the hydrogen atom. ( $R_H = 1.09678 \times 10^7 \text{ m}^{-1}$ ,  $h = 6.6256 \times 10^{-34} \text{ J-s}$ )

**Solution**  $n_1 = 1$ ,  $n_2 = \infty$

$$\frac{1}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right).$$

$$\frac{1}{\lambda} = 1.09678 \times 10^7 \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right).$$

$$\lambda = 9.11 \times 10^{-8} \text{ m}$$

$$E = hv = h \times c/\lambda$$

$$(C = 3 \times 10^8 \text{ m sec}^{-1})$$

$$= \frac{6.6256 \times 10^{-34} \times 3 \times 10^8}{9.11 \times 10^{-8}}$$

$$= 2.18 \times 10^{21} \text{ kJ}.$$

15. Calculate (in  $\text{kJ mol}^{-1}$ ) the energy necessary to remove an electron from the first shell of a hydrogen atom. Given:  $R = 1.097 \times 10^{-2} \text{ nm}^{-1}$ .

**Solution**  $n_1 = 1$ ,  $n_2 = \infty$ ,  $R = 1.097 \times 10^{-2} \text{ nm}^{-1}$

$$\frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right).$$

$$= R \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right)$$

$$= R (1/1)$$

$$= 1.097 \times 10^7 \text{ m}$$

$$\text{so } \lambda = \frac{1}{1.097 \times 10^7} = 0.912 \times 10^{-7} \text{ m}$$

$$= 912 \text{ Å}$$

$$E = \frac{hc}{\lambda} \times N_0$$

$$= \frac{6.626 \times 10^{-34} \times 10^8 \times 6.023 \times 10^{23}}{912 \times 10^{-10}}$$

$$= 1.31 \times 10^6 \text{ J mol}^{-1} = 1310 \text{ kJ}$$

16. Calculate the energy emitted when electrons of  $1.0 \text{ g}$  atom of hydrogen undergo transition giving the spectral lines of lowest energy in the visible region of its atomic spectra. Given:  $R_H = 1.1 \times 10^7 \text{ m}^{-1}$ ,  $c = 3 \times 10^8 \text{ m sec}^{-1}$ ,  $h = 6.62 \times 10^{-34} \text{ sec}$ .

**Solution** Visible line spectrum nearly Balmer series that is,

$n_1 = 2$  and for minimum energy transition  $n_2 = 3$ .

$$\text{As } \frac{1}{\lambda} = R_H Z \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right).$$

[as  $Z = 1$ ]

$$\text{So } \frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{3^2} \right).$$

$$= 1.1 \times 10^7 \left( \frac{1}{4} - \frac{1}{9} \right)$$

### 3.14 ■ Atomic Structure

$$= 1.1 \times 10^7 \times \frac{5}{36} = 6.55 \times 10^{-7} \text{ metre}$$

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{6.55 \times 10}$$

$$= 3.034 \times 10^{-19} \text{ J}$$

Suppose  $N_0$  electrons show this transition in 1 g atom of H then

$$\text{Energy released} = E \times N_0$$

$$= 3.034 \times 10^{-19} \times 6.023 \times 10^{23}$$

$$= 18.29 \times 10^4 \text{ J}$$

$$= 182.9 \text{ kJ.}$$

17. Calculate the ionization energy in kJ per mole for the removal of the valence electron from a hydrogen atom. Compare your answer with the experimentally accepted value of 1312 kJ mol<sup>-1</sup>.

#### Solution

$$\text{Here } n_1 = 1, n_2 = \infty$$

$$R_H = 2.18 \times 10^{-21} \text{ kJ.}$$

$$\Delta E = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right).$$

$$\Delta E = 2.18 \times 10^{-21} \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right).$$

$$\Delta E = 2.18 \times 10^{-21} \text{ kJ per electron}$$

$$\text{As in one mole number of electrons} = 6.02 \times 10^{23}$$

$$\text{So for 1 mole } \Delta E = 2.18 \times 10^{-21} \times 6.023 \times 10^{23}$$

$$= 1.31 \times 10^3 \text{ kJ}$$

$$= 1310 \text{ kJ}$$

This value is nearly equal to accepted value 1312 kJ.

#### De Broglie Equation and Dual Nature Theory

- De Broglie introduced dual nature theory for matter that is, for sub atomic particle ( $e^-$ , p, n). According to it, matter has both particle as well as wave nature. Wave nature of electron was confirmed by Devisson and Germer on diffraction pattern experiment on nickel surface like X-rays.

de Broglie used Einstein theory and Plank theory to give the following equation:

$$E = mc^2 \text{ for particle}$$

$$E = h\nu \quad \text{for wave}$$

$$E = \frac{hc}{\lambda}$$

$$\frac{hc}{\lambda} = mc^2$$

$$\frac{1}{\lambda} = \frac{mc^2}{hc}$$

$$\lambda = \frac{h}{mc}.$$

If  $c = v$ .

$$\lambda = \frac{h}{mv}.$$

$$\lambda = \frac{h}{p} \quad (\text{As } p = mv)$$

$$\lambda \propto \frac{1}{p} \quad \text{at constant temperature}$$

- If a particle has more mass or momentum, it has less wavenature. Heavy objects have less wavelength due to more mass.

E.g.,  $e > p > n > > \dots$  Cricket ball

#### Derivation of Bohr's postulate

According to de Broglie's equation

$$\lambda = \frac{h}{mv}.$$

As an electron in a circular path must have its path length (circumference =  $2\pi r$ ) equal to an integral multiple of wavelength so

$$2\pi r = n \cdot \lambda$$

$$2\pi r = n \cdot \frac{h}{mv}.$$

$$mv = n \cdot \frac{h}{2\pi}.$$

So angular momentum of an electron is simple multiple of  $h/2\pi$ .

#### Relation between Wave Length and Kinetic Energy

$$\boxed{\lambda = \frac{h}{\sqrt{2mK.E}}}$$

As  $K.E = \frac{1}{2}mv^2 = e.V$  potential difference

$$\frac{1}{2}mv^2 = e.V$$

$$v^2 = 2 \frac{e.V}{m}$$

$$v = \sqrt{2e.V/m}$$

$$\text{So } \lambda = \frac{h}{\sqrt{2m e.V}}$$

For electron:

$$\lambda = \frac{12.27}{\sqrt{V}} \text{ Å}$$

For proton:

$$\lambda = \frac{0.286}{\sqrt{V}} \text{ Å}$$

For  $\alpha$  - particles:

$$\lambda = \frac{0.101}{\sqrt{V}} \text{ Å}$$

## Illustrations

18. Find the wavelength of a 150 g rubber ball moving with a velocity 50 m sec<sup>-1</sup>. ( $h = 6.62 \times 10^{-34}$  Js).

**Solution**  $\lambda = \frac{h}{mv} = \frac{6.62 \times 10^{-34}}{0.150 \times 50} = 8.82 \times 10^{-35} \text{ m}$   
 $= 8.82 \times 10^{-33} \text{ cm}$

19. Calculate the momentum of a moving particle which has a de Broglie wave length of 2 Å.

**Solution** According to de Broglie equation

$$\lambda = \frac{h}{p}$$

$$p = \frac{h}{\lambda}$$

$$= \frac{6.62 \times 10^{-34}}{2 \times 10^{-10}} = 3.31 \times 10^{-24} \text{ Kg ms}^{-1}$$

## Heisenberg Uncertainty Principle

It is applicable only for sub atomic microscopic particles.

According to it, it is impossible to measure simultaneously and correctly both change in position and change in momentum that is, if one thing is certain another is uncertain. It is also called principle of indeterminacy.

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \cdot m \cdot \Delta v \geq \frac{h}{4\pi}$$

Here  $\Delta x$  = uncertainty in position

$\Delta v$  = uncertainty in velocity

$$\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$$

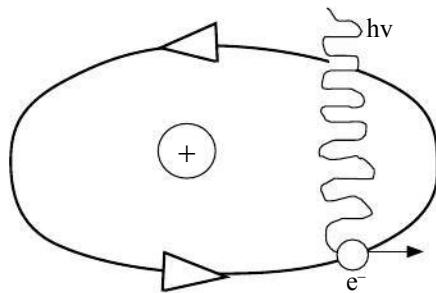
$$\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

here  $\Delta E$  = change in energy

$\Delta t$  = change in time

- If change in position is zero change in momentum will be infinite and vice versa.
- It applies when both  $\Delta x$  and  $\Delta P$  are along with the same axis.
- In case of larger objects, the value of uncertainty principle is negligible if the position is known quite accurately ( $\Delta x$  is very small) there will be great uncertainty in the velocity ( $\Delta v$  is very large)

An  $e^-$  cannot exist within the nucleus as using this principle  $\Delta v$  is  $5.8 \times 10^{10}$  m/sec that is 200 time of velocity of light which is not possible.



## Illustrations

20. Calculate the uncertainty in position of an electron whose velocity is  $3.0 \times 10^4$  cm s<sup>-1</sup> accurate upto 0.001 %. Mass of an electron =  $9.1 \times 10^{-28}$  g.

**Solution**  $\Delta v = \frac{0.001}{100} \times 3.0 \times 10^4 \text{ cm s}^{-1}$

$$= 0.3 \text{ cm s}^{-1}$$

$$\text{As } \Delta x = \frac{h}{4\pi (m\Delta v)} .$$

$$= \frac{6.626 \times 10^{-34} \text{ erg s}}{4 \times 3.14 \times 9.1 \times 10^{-28} \text{ g} \times 0.3 \text{ cm s}^{-1}} .$$

$$= 1.92 \text{ cm} \quad (\text{As erg} = \text{g cm}^2 \text{ s}^{-2})$$

21. A cricket ball weighing 100 g is to be located with 0.1 Å. What is the uncertainty in its velocity?

### 3.16 ■ Atomic Structure

**Solution**  $\Delta x \cdot m \Delta v = \frac{h}{4\pi}$

$$\Delta x = \text{Location of ball} = 0.1\text{\AA} = 0.1 \times 10^{-10} \text{ m}$$

$$m = \text{Mass of ball} = 100 \text{ g} = 0.1 \text{ kg}$$

$\Delta v$  = Uncertainty in velocity

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$0.1 \times 10^{-10} \times 0.1 \times \Delta v = \frac{6.626 \times 10^{-34}}{4 \times 3.14}$$

$$\Delta v = 0.527 \times 10^{-22} \text{ ms}^{-1}$$

### Concept of Probability

As the position and momentum of an electron can not be found accurately at a particular time so the idea of definite orbits (sharply defined path) as suggested by Bohr has no meaning now for a moving electron in an atom. Hence the concept of probability was developed.

According to it, it is possible to predict or state the probability on locating an electron of a particular energy in a given region of space around the nucleus at a given time. This leads the concept of orbital.

### Schrodinger Wave Equation

Schrodinger set up a mathematical model for hydrogen atom. This theory was based upon these two evidences:

- (i) The probability or statistical character
- (ii) The wave nature of an electron

The schrodinger's wave equation plains three dimensional wave nature of electron as follows

$$\frac{\delta^2 \psi}{\delta X^2} + \frac{\delta^2 \psi}{\delta Y^2} + \frac{\delta^2 \psi}{\delta Z^2} + \frac{8\pi^2 m}{h^2} [E - V] \psi = 0$$

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} [E - V] \psi = 0$$

Here X, Y, Z are three co-ordinate axis, E is total energy, V is potential energy ( $V = -Ze^2/r$ ), m is mass of electron wave and  $\nabla^2 \psi$  is laplation operature.

This equation possesses a number of solutions each corresponding to a discrete energy state and

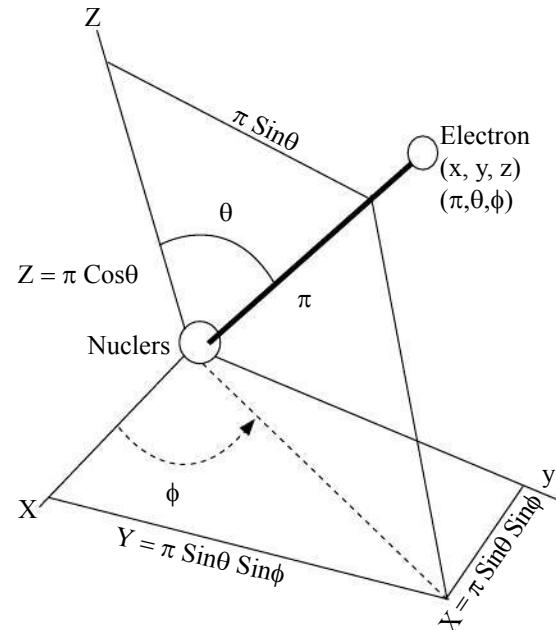
specified by the values of three quantum numbers n, l, m. The solutions have significance for certain definite values of total energy 'E'. These values are known as Eigen values and for an atom these values correspond to discrete sets of energy values postulated by the Bohr's theory.

### Significance of $\psi$ and $\psi^2$

$\psi$ : It has no physical significance. It represent amplitude of electron wave or boundary surface of an orbital.

$\psi^2$ : It is probable electron density or It is probability of finding electron in any region (3 dimensional around the nucleus). If  $\psi^2$  is positive electron are present and if  $\psi^2$  is zero electrons are absent.

- An orbital is represented by  $\psi$ ,  $\psi^*$  or  $\psi^2$  for showing electron density.
- The probability of finding electron at a distance r from the nucleus in the region dr is given by  $4\pi r^2 dr \psi^2$ .



- Schrodinger gave another equation when energy of an atom or molecule does not change which is written as

^

$$H \psi = E \psi$$

^

$$H = \left[ -\frac{\hbar^2}{8\pi^2 m} \nabla^2 + V \right]$$

$$H = \left[ -\frac{\hbar^2}{8\pi^2 m} \nabla^2 + V \right]$$

$$\text{As } \hat{H} = \hat{T} + \hat{V}$$

$$\text{So } (\hat{T} + \hat{V})\psi = E\psi$$

Here  $H$  = Hamiltonian factor

$V$  = Potential energy

$T$  = Kinetic energy

$E$  = Total energy

## Orbital

It is the three dimensional region of high electron density that is high probable electron density region having different shapes around the nucleus.

- The probability of finding an electron in any orbital is more than 90 per cent.
- An orbital is a mathematical function of the three co-ordinate  $r$ ,  $\theta$  and  $\phi$ . which can be factorized into 3-separate parts each of which is a function of only one co-ordinate as follows

$$\Psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi)$$

Here:

$R(r)$ : Radial function which depends upon  $n$ ,  $l$  value and it shows dependence of an orbital upon distance  $r$  of electron from nucleus.

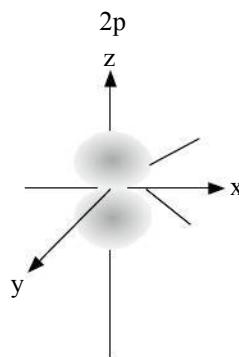
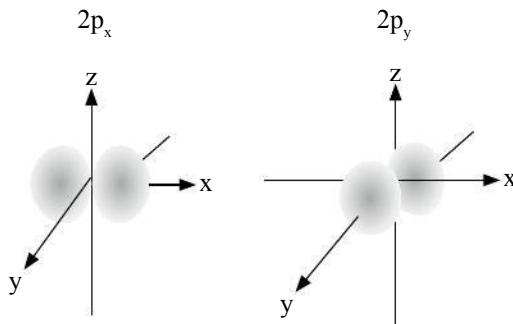
$\Theta(\theta)$  and  $\Phi(\phi)$ : It is angular function depending upon  $l$ ,  $m$  values. It shows angular dependence of orbital on  $\theta$  and  $\phi$  respectively.

that is,

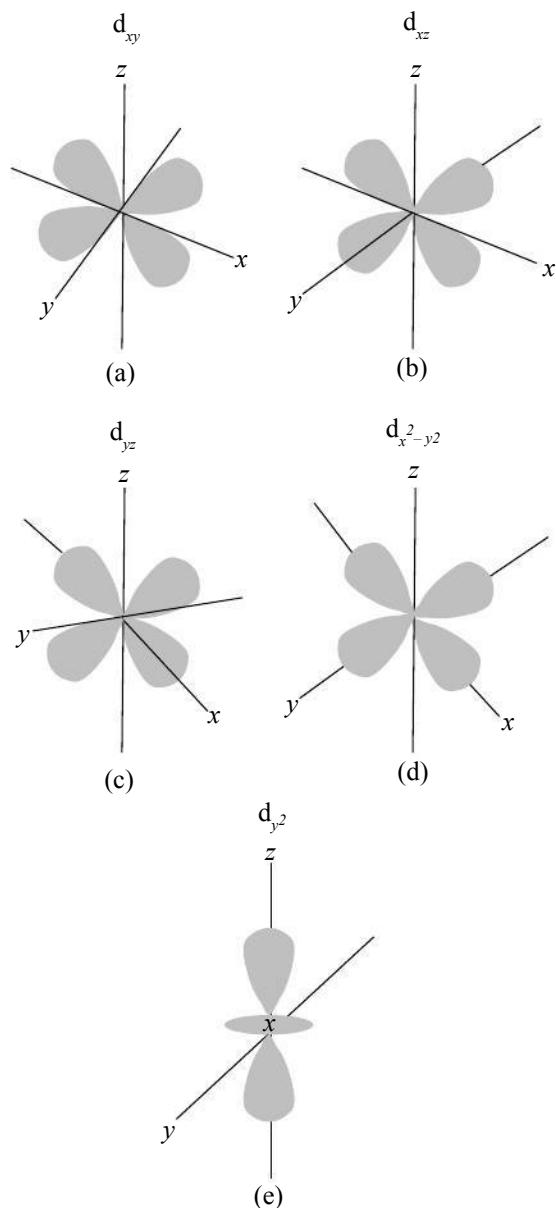
$$\Psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r) \Theta_{l,m}(\theta) \Phi_m(\phi)$$

radial part	angular part
-------------	--------------

## Shape of Orbitals



Boundary surface diagrams of the three 2p orbitals.



### Some Facts about Orbitals

- Orbital represents both particle and wave nature of electron.
- It is directional in nature (except s-orbital).
- Any orbital can have maximum two electrons and these electrons are with opposite or antiparallel spin.
- $dz^2$  orbital has only two lobes lying along with z axis and a drought on x and y axis. Its shape is baby schooter type.
- In  $dx^2y^2$  all the four lobes are lying along with molecular axis that is, x and y.

### Degenerate Orbital

Orbitals with same value of n and of same sub shell are degenerate orbitals.

Example, –  $2px$ ,  $2py$ ,  $2pz$   
 $3dxy$ ,  $3dyz$ ,  $3dxz$ .

### Radial Probability Distribution Function

- It is the probability of finding electrons in the region between  $r$  and  $dr \delta r$ . It is given by  $4\pi r^2 \psi^2 \delta r$ . It is directional independent.

Here  $r$  = radius or distance from nucleus  
 $\delta r$  = thickness

### Node

It is zero electron density region.

$$\psi^2 = 0$$

### Radial Node

It is region between two successive 's' orbitals.

### Nodal Point

It is a point where two lobes are joint and electron density is zero here.

### Nodal Planes

It is plane by which two lobes are separated and electron density is zero here.

- Any s-orbital has no nodal plane or point.
- $px$ ,  $py$ ,  $pz$ ,  $dz^2$  orbitals have one nodal plane or point.
- Rest of d-orbitals ( $dxy$ ,  $dyz$ ,  $dxz$ ,  $dx^2 - y^2$ ) have two nodal plane or points.

### Calculation of Nodes

$$\text{Node} = n - 1$$

$$\text{Radial nodes or spherical nodes} = n - l - 1$$

$$\text{Angular or non-spherical} = l$$

$$\text{Example, } 1s: \text{Node} = 1 - 1 = 0$$

$$\text{Example, } 2s: \text{Node} = 2 - 1 = 1$$

$$\text{Angular node} = 0$$

$$\text{Radial node} = 2 - 0 - 1 = 1$$

$$\text{Example, } 3s: \text{Node} = 3 - 1 = 2$$

$$\text{Angular node} = 0$$

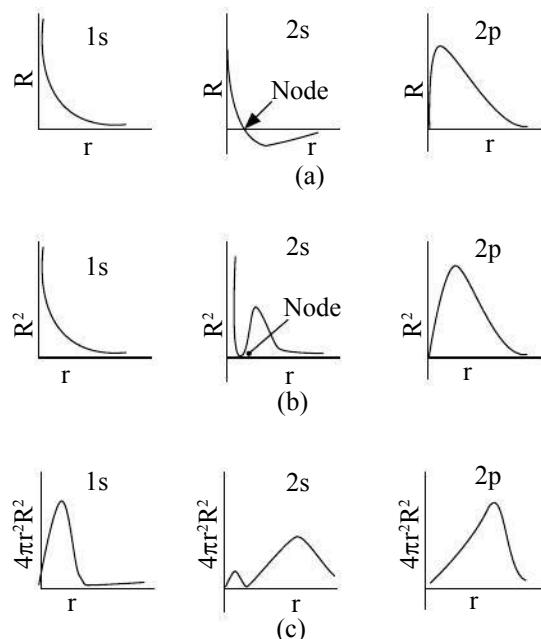
$$\text{Radial node} = 3 - 0 - 1 = 2$$

$$\text{Example, } 4d: \text{Node} = 4 - 1 = 3$$

$$\text{Angular node} = 0$$

$$\text{Radial node} = 4 - 0 - 1 = 3$$

### Various Probability Curves



The plots of (a) the radial wave function  $R$ ; (b) the radial probability density  $R^2$  and (c) the radial density function  $4\pi r^2 R^2$  as a function of distance  $r$  of the electron from the nucleus for 1s, 2s and 2p orbitals. The plots are not drawn to scale.

## QUANTUM NUMBERS

These are set of four numbers used to address electron as follows:

- To determine size, distance from nucleus and energy of electron in orbit.
- To decide shape, energy of electron in sub orbit.
- To find number of orbitals and their directional position or orientation in space.
- To find number of electrons and their spin.

### Principle Quantum Number

It was introduced by Bohr and it is denoted by 'n'. It determines:

- Size of orbit (shell)
- Distance of orbit from nucleus
- Energy of electron in an orbit.
- Maximum number of electrons in any orbit
- Angular momentum of electron in an orbit

$$mvr = \frac{n\hbar}{2} = n\hbar$$

$mvr$  = angular momentum in orbit.

$h$  = plank's constant

Values of  $n = 1, 2, 3, 4, \dots, \infty$

$n \neq 0, -ve, \text{ fractional}$

### Azimuthal or Secondary or Angular Momentum Quantum Number

It was introduced by Sommerfeld and denoted by 'l'.

It determines shape of sub orbit, energy in sub shell and angular momentum of an electron in any orbital

Angular momentum of an electron in any orbital is given as:

$$mvr = \sqrt{l(l+1)} \frac{\hbar}{2\pi} \text{ or } \hbar$$

Example, For any s orbital  $e^-$  ( $mvr$ ) = 0 (as  $l = 0$ )

$$\text{For any p orbital } e^- (\text{mvr}) = \sqrt{1(1+1)} \hbar \\ = \sqrt{2}\hbar$$

$$\text{For any d orbital } e^- (\text{mvr}) = \sqrt{2(2+1)} \hbar \\ = \sqrt{6}\hbar$$

$$\text{For any f orbital } e^- (\text{mvr}) = \sqrt{3(3+1)} \hbar \\ = \sqrt{12}\hbar$$

It explains the existence of many closely packed spectrum lines in hydrogen spectrum.

### ■ Values of $l = 0$ to $n - 1$

Example,

n :	1	2	3	4
l :	0	0, 1	0, 1, 2	0, 1, 2, 3

l-value:	0	1	2	3	4
suborbit	s	p	d	f	g

### Magnetic Quantum Number

It was introduced by Land and Zeeman and is denoted by m.

It determines:

- Number of orbitals = total m values =  $n^2$  (when n is given)  
 $= 2l + 1$  when 'l' is given.

Example, – when  $n = 2$

$$m (\text{total}) = 2^2 = 4$$

when  $l = 2$

$$m (\text{total}) = 2 \times 2 + 1 = 5$$

- Directional position of orbitals or orientation in shape and Zeemann effect.

- Angular magnetic momentum

$$mvr = m \frac{\hbar}{2} = m\hbar$$

Values of m =  $-l$  to  $+l$  including zero.

Example,  $l=0, m=0$

$$l=1, m=-1, 0, +1$$

$$l=2, m=-2, -1, 0, +1, +2$$

### Spin Quantum Number

It was introduced by Uhlenbeck and Goud Smith. It is the intrinsic angular momentum measurement which is used to differentiate between two electrons in an orbital that is, it explains the fine structure of the spectral lines within atomic levels.

Spin angular momentum is given as:

$$mvr = \sqrt{s(s+1)} \frac{\hbar}{2\pi} \text{ or } \hbar$$

The electron in an atom rotates not only around the nucleus but also rotates around its own axis and this rotation is called spin of the electron.

## 3.20 ■ Atomic Structure

- For each value of  $m_l$ ,  $s$  has two different values +  $\frac{1}{2}$  and -  $\frac{1}{2}$ .

$$\begin{array}{ll} +\frac{1}{2} & -\frac{1}{2} \\ \alpha - \text{spin} & \beta - \text{spin} \end{array}$$

- +  $\frac{1}{2}$  and -  $\frac{1}{2}$  are just to mechanical spin states with no classical importance now as other spin states are also possible. (Bosons and fermions)

### Values of $s$

Total values of 's' or total number of electrons =  $2m_s = 2n^2 = 2(l+1)$

- Schrodinger cannot explain spin of electron and spin quantum number.

### REMEMBER

Orbital Orbital function

$$1s \quad \frac{1}{\sqrt{\pi}} a_o^{-3/2} e^{-p}$$

$$2s \quad \frac{1}{4\sqrt{\pi}} a_o^{-3/2} (2-p) e^{-p/2}$$

$$2p_z \quad \frac{1}{4\sqrt{\pi}} a_o^{-3/2} P e^{-p/2} \cos\theta$$

$$2p_x \quad \frac{1}{4\sqrt{\pi}} a_o^{-3/2} P e^{-p/2} \sin\theta \cos\theta$$

$$2p_y \quad \frac{1}{4\sqrt{\pi}} a_o^{-3/2} e^{-p/2} \sin\theta \sin\theta$$

### Illustration

22. Write the suitable combinations of quantum numbers for each of the following electrons:
- A 4s electron
  - A 3p electron
  - A 5f electron
  - A 5d electron

**Solution** (a) 4s,  $n = 4$ ;  $l = 0$ ;  $m_l = 0$ ;  $m_s = \pm \frac{1}{2}$

(b) 3p,  $n = 3$ ;  $l = 1$ ;  $m_l = -1, 0, +1$ ;  $m_s = \pm \frac{1}{2}$

(c) 5f,  $n = 5$ ;  $l = 3$ ;  $m_l = -3, -2, -1, 0, +1, +2, +3$ ;  $m_s = \pm \frac{1}{2}$

(d) 5d,  $n = 5$ ;  $l = 2$ ;  $m_l = -2, -1, 0, +1, +2$ ;  $m_s = \pm \frac{1}{2}$

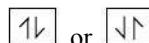
## Electronic Configuration

It represents the distribution of electrons in various orbits, sub-orbits and orbitals in order to understand electronic behaviour. For the filling of electrons in various orbitals following three rules are considered.

### Pauli Exclusion Principle

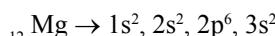
It has following two statements:

- Any orbital can have maximum two electrons and these electrons must have opposite or anti-parallel spin.



- No two electrons of an atom can have a same set of all the four quantum numbers. If  $n, l, m$  are same 's' is definitely different.

E.g.,



$n \quad l \quad m \quad s$

for 11<sup>th</sup>  $e^- \rightarrow 3 \quad 0 \quad 0 \quad +\frac{1}{2}$

for 12<sup>th</sup>  $e^- \rightarrow 3 \quad 0 \quad 0 \quad -\frac{1}{2}$

### Uses of Pauli's Law

To find maximum number of electrons in any orbit, sub orbit and orbital as follows

- Orbit: Maximum number of electrons =  $2 n^2$

$$n = 1 \text{ for K } e^- = 2 \times 1^2 = 2e^-$$

$$n = 2 \text{ for L } e^- = 2 \times 2^2 = 8e^-$$

$$n = 3 \text{ for M } e^- = 2 \times 3^2 = 18 e^-$$

- In Sub orbit :

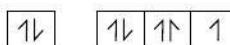
s	p	d	f	g
2	6	10	14	18

- Orbital : Maximum two electrons are possible in any orbital.

E.g.,  $p_x, p_y, p_z, d_z^2$

### Violation of Pauli's Law

When electronic spin is same in any degenerate orbital the law is violated.



Example,

It is also violated when electrons are filled even after a maximum limit example.  $1s^7$  configuration for nitrogen cannot be written because in 1<sup>st</sup> orbit only Max  $2e^-$  can exist and any s-subshell can have two electrons.

**Aufbau's Principle:** It is a German word which means to build so it is also called building up rule. It states that as protons are added one by one to the nucleus to build by elements, electrons are similarly added to  $(n+l)$  rule.

### **$(n+l)$ Rule**

According to it electrons are filled in different orbitals from lower  $(n+l)$  value orbital to higher  $(n+l)$  value orbital as follows:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s, < 4f < 5d < 6p < 7s < 5f < 6d$$

Increasing order of  $n+l$  value or energy.

**In case  $(n+l)$  value is same** Electron is filled first in orbital with lower value of n.

Example, 3p,                  4s  
n = 3                  n = 4

In case of Hydrogenic species energy depends only upon 'n'-value

$$\text{So } 1s < 2s = 2p < 3s = 3p = 3d <$$

### **To Write Electronic Configuration**

- First fill electrons in orbital according to  $(n+l)$  rule (initial configuration).
- If atomic number is  $> 20$  arrange the orbitals/sub-orbitals in the increasing order of n-value (for final configuration).

Example,  $_{26}\text{Fe}$

$$1s^2, 2s^2 2p^6 3s^2 3p^6, 4s^2, 3d^6$$

$$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6, 4s^2$$

(final configuration)

S.No.	Elements	Symbol	Atomic number	Electronic configuration
1	Hydrogen	H	1	$1s^1$
2	Helium	He	2	$1s^2$
3	Lithium	Li	3	$1s^2, 2s^1$
4	Beryllium	Be	4	$1s^2, 2s^2$
5	Boron	B	5	$1s^2, 2s^2 2p^1$
6	Carbon	C	6	$1s^2, 2s^2 2p^2$
7	Nitrogen	N	7	$1s^2, 2s^2 2p^3$
8	Oxygen	O	8	$1s^2, 2s^2 2p^4$
9	Fluorine	F	9	$1s^2, 2s^2 2p^5$
10	Neon	Ne	10	$1s^2, 2s^2 2p^6$
11	Sodium	Na	11	$1s^2, 2s^2 2p^6, 3s^1$
12	Magnesium	Mg	12	$1s^2, 2s^2 2p^6, 3s^2$
13	Aluminium	Al	13	$1s^2, 2s^2 2p^6, 3s^2 3p^1$
14.	Silicon	Si	14	$1s^2, 2s^2 2p^6, 3s^2 3p^2$
15.	Phosphorous	P	15	$1s^2, 2s^2 2p^6, 3s^2 3p^3$

### 3.22 ■ Atomic Structure

S.No.	Elements	Symbol	Atomic number	Electronic configuration
16	Sulphur	S	16	$1s^2, 2s^2 2p^6, 3s^2 3p^4$
17	Chlorine	Cl	17	$1s^2, 2s^2 2p^6, 3s^2 3p^5$
18	Argon	Ar	18	$1s^2, 2s^2 2p^6, 3s^2 3p^6$
19	Potassium	K	19	$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^1$
20	Calcium	Ca	20	$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2$
21	Scandium	Sc	21	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1, 4s^2$
22	Titanium	Ti	22	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^2, 4s^2$
23	Vanadium	V	23	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^3, 4s^2$
24	Chromium	Cr	24	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$
25	Manganese	Mn	25	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^2$
26	Iron	Fe	26	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6, 4s^2$
27	Cobalt	Co	27	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^7, 4s^2$
28	Nickel	Ni	28	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^8, 4s^2$
29	Copper	Cu	29	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$
30	Zinc	Zn	30	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2$
31	Gallium	Ga	31	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^1$
32	Germanium	Ge	32	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^2$
33	Arsenic	As	33	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^3$
34	Selenium	Se	34	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^4$
35	Bromine	Br	35	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^5$
36	Krypton	Kr	36	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6$

### Some Exceptional Configurations

In case of fully filled and half filled orbitals, stability is more due to more exchanges, exchange energy and symmetry. ( $d^5 > d^4$  and  $d^{10} > d^9$ )

### Exchange Energy

It is defined as the amount of energy needed to exchange the positions of electrons having same spin. Hence every exchange decreases the energy of

the system and provides the stability to the system. Let each exchange associates with energy A so total decrease in energy of the system =  $\Delta E = N \times A$ . Here N = Total number of exchanges.

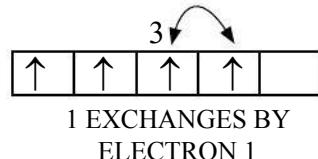
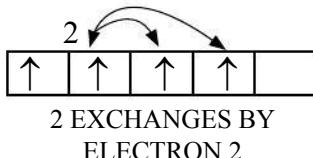
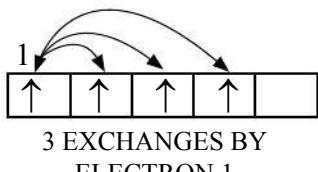
$$N = \frac{r!}{2(r-2)!} + \frac{s!}{2(s-2)} .$$

Here

r = Number of electrons having clockwise direction

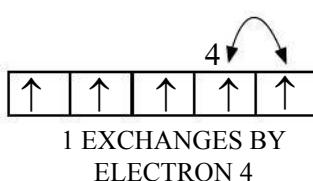
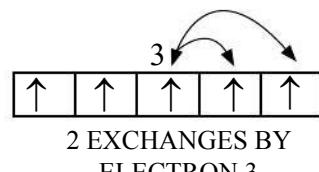
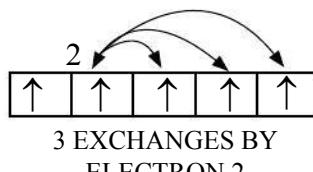
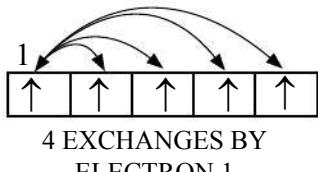
s = Number of electrons anticlockwise direction

The number of exchanges that can take place in  $d^4$  configuration are as follows:



$$\text{Total number of exchanges} = 3 + 2 + 1 = 6$$

The number of exchanges that can take place in  $d^5$  configuration are as follows:

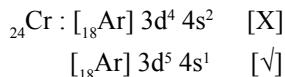


$$\text{Total number of exchanges} = 4 + 3 + 2 + 1 = 10$$

### Case I:

$(n - 1)d^4, ns^2$  :  $(n - 1)d^5, ns^1$   
incomplete              both orbitals are half  
d-orbital so            filled so more stable.  
Less stable

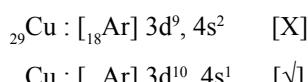
Example—



### Case II:

$(n - 1)d^9 ns^2$  :  $(n - 1)d^{10} ns^1$   
incomplete              full        half  
d-orbital so            filled      filled  
less stable              more stable

Example—



### Some Other Exceptional Configurations

<sub>41</sub>Nb:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^4 5s^1$   
<sub>42</sub>Mo:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5 5s^1$   
<sub>44</sub>Ru:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$   
 $4p^6 4d^7 5s^1$

or

[Kr]  $4d^7 5s^1$

<sub>45</sub>Rh: [Kr]  $4d^8 5s^1$

<sub>46</sub>Pd: [Kr]  $4d^{10} 5s^0$

<sub>47</sub>Ag: [Kr]  $4d^{10} 5s^1$

<sub>57</sub>La: [Xe]  $4f^0 5d^1 6s^2$

<sub>58</sub>Ce: [Xe]  $4f^2 5d^0 6s^2$

<sub>61</sub>Pm: [Xe]  $4f^5 5d^0 6s^2$

<sub>78</sub>Pt: [Xe]  $4f^{14} 5d^9 6s^1$

<sub>79</sub>Au: [Xe]  $4f^{14} 5d^{10} 6s^1$

### 3.24 ■ Atomic Structure

These exceptions are mainly because of interaction between nucleus and valence electron.

#### Violation of Aufbau Rule

1	1	1	1
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As in p-subshell electrons can be filled after completing the maximum limit of electrons in s-subshell.

#### Hund's Rule of Maximum Multiplicity

According to it, "In degenerate orbitals, electron are filled in such a way so that maximum stability and multiplicity can be obtained for it first each degenerate orbital is singly occupied than pairing of electron takes place", or, The most stable arrangement of electrons in sub-orbits is the one with the greatest number of parallel spins.

#### Hund's Violation

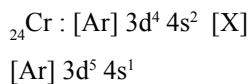
1	1	1	
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pairing empty degenerate orbital

#### Uses:

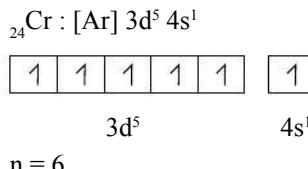
- To write the correct and stable electronic configuration

Example,



- To find number of unpaired electrons (n)

Example,



- To find multiplicity (m) :

$$m = (n + 1) = (2s + 1), \quad (s = \frac{n}{2})$$

Example—



$$m = 6 + 1 = 7$$

- Number of spins =  $n/2 = 6/2 = 3$ .

- To find magnetic nature and magnetic moment:

$n = 0$  diamagnetic

$n = 1, 2, 3$  paramagnetic

$n = 4, 5, 6$  ferromagnetic or highly paramagnetic

magnetic moment ( $\mu$ ) =  $\sqrt{n(n+2)} B.M$

B.M. = Bohr magneton

#### To Find Colour

- If  $n = 0$  ion is colourless

Example,—  $\text{Cu}^+$ ,  $\text{Zn}^{+2}$ ,  $\text{Cd}^{+2}$

- If  $n = 1, 2, 3$  ion is coloured

Example,  $\text{Cu}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$

Config- uration	n	$\mu$ in B.M	spin	examples
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$d^1$ or $d^9$	1	$\sqrt{3}$	1/2	$\text{Cu}^{2+}$ , $\text{Sc}^{+2}$
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$d^2$ or $d^8$	2	$\sqrt{8}$	1	$\text{Ti}$ , $\text{Ti}^{+2}$ , $\text{Ni}$ , $\text{Ni}^{+2}$
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$d^3$ or $d^7$	3	$\sqrt{15}$	3/2	$\text{V}$ , $\text{V}^{+2}$ , $\text{Co}$ , $\text{Co}^{+2}$ , $\text{Cr}^{+3}$
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$d^4$	4	$\sqrt{24}$	2	$\text{fe}$ , $\text{fe}^{+2}$ , $\text{Cr}^{2+}$
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$d^5$	5	$\sqrt{35}$	5/2	$\text{mn}$ , $\text{fe}^{3+}$ , $\text{mn}^{2+}$
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#### Illustration

23. A compound of Nickel has a magnetic moment of 2.79 BM. Write the electronic configuration of the chromium ion in this compound.

**Solution** As  $\mu = \sqrt{n(n+2)}$

$$2.79 = \sqrt{n(n+2)}$$

On solving,

$$n = 2$$

As there are two unpaired electrons so Ni is in  $\text{Ni}^{2+}$  state. Hence its configuration is written as



#### Enhance Your Knowledge

- The radius, r of the nucleus of an atom is related to its mass number(A) according to the equation

$$r = R_0 A^{1/3}$$

where  $R_0$  is a constant having value  
 $= 1.4 \times 10^{-15} \text{ m}$ .

- The shapes of the seven f-orbitals are complicated but their designations are as follows.

$$fx^3, fy^3, fz^3, fx(z^2 - y^2), fy(z^2 - x^2), fz(y^2 - x^2), fxyz.$$

- These are not possible  $n \neq 1, n < 1, m \geq 1$ . If any of these is not obeyed arrangement of quantum numbers set is not permissible.
- Since l can not be equal to n so orbitals  $1p, 2d, 3f, 4g$  do not exist.

### Solved Problems from the IITs

1. Calculate the wavelength in Angstroms of the photon that is emitted when an electron in Bohr orbit  $n = 2$  returns to the orbit  $n = 1$  in the hydrogen atom. The ionization potential of the ground state of hydrogen atom is  $2.17 \times 10^{-11}$  erg per atom.

[IIT 1982]

**Solution** Ionization potential of the ground state of hydrogen atom is  $2.17 \times 10^{-11}$  erg.

$$E_1 = -2.17 \times 10^{-11} \text{ erg}$$

$$E_2 = \frac{-2.17 \times 10^{-11} \text{ erg}}{2^2}$$

$$E_2 = -0.5425 \times 10^{-11} \text{ erg}$$

$$E_2 - E_1 = 1.6275 \times 10^{-11} \text{ erg}$$

$$E_2 - E_1 = h\nu = hc/\lambda$$

$$\lambda = \frac{hc}{E_2 - E_1}$$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{1.6275 \times 10^{-11}}$$

$$= 1221 \times 10^{-10} \text{ m} = 1221 \text{ Å}$$

2. According to Bohr's theory, the electronic energy of the hydrogen atom in the  $n$ th Bohr's orbit is given by

$$E_n = -\frac{21.76 \times 10^{-19} \text{ J}}{n^2}$$

Calculate the longest wavelength of light that will be needed to remove an electron from the third orbit of the  $\text{He}^+$  ion.

[IIT 1990]

**Solution** The electronic energy of  $\text{He}^+$  ion in the  $n$ th Bohr orbit

$$= -\frac{21.76 \times 10^{-19} \times Z^2 \text{ J}}{n^2}$$

Here  $Z = 2$

So energy of  $\text{He}^+$  in the third Bohr orbit

$$= -\frac{21.76 \times 10^{-19} \times 4 \text{ J}}{9}$$

$$\Delta E = E_\infty - E_3$$

$$= 0 - \frac{[-21.76 \times 10^{-19} \times 4]}{9}$$

$$= \frac{21.76 \times 10^{-19} \times 4}{9}$$

$$\text{As } \lambda = \frac{hc}{\Delta E}$$

$$= \frac{6.625 \times 10^{-34} \times 3 \times 10^8 \times 9}{21.76 \times 10^{-19} \times 4}$$

$$= 2.055 \times 10^{-7} \text{ m}$$

3. Estimate the difference in energy between the first and second Bohr orbit for hydrogen atom. At what minimum atomic number would a transition from  $n = 2$  to  $n = 1$  energy level result in the emission of X-rays with  $\lambda = 3.0 \times 10^{-8} \text{ m}$ ? Which hydrogen like species does this atomic number correspond to?

[IIT 1993]

**Solution**  $\Delta E = h\nu = \frac{hc}{\lambda}$

$$\frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\Delta E = R.h.c \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

### 3.26 ■ Atomic Structure

$$\Delta E = h \cdot c \cdot \frac{3}{4} R$$

$$= \frac{6.625 \times 10^{-34} \times 3 \times 10^8 \times 1.09678 \times 10^7 \times 3}{4}$$

$$= 1.635 \times 10^{-18} \text{ J}$$

For hydrogen like species

$$\Delta E = Z^2 R \cdot h \cdot c \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\frac{1}{\lambda} = Z^2 R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\frac{1}{3.0 \times 10^{-8}} = Z^2 \times 1.09678 \times 10^7 \times \left[ \frac{1}{1^2} - \frac{1}{2^2} \right]$$

$$Z^2 = \frac{4}{3 \times 10^{-8} \times 1.09678 \times 10^7 \times 3} = 4$$

$$Z = 2$$

Hence the species is  $\text{He}^+$ .

4. The dipole moment of  $\text{KCl}$  is  $3.336 \times 10^{-29}$  coulomb meter which indicates that it is a highly polar molecule. The interatomic distance between  $\text{K}^+$  and  $\text{Cl}^-$  in this molecule is  $2.6 \times 10^{-10}$  m. Calculate the dipole moment of  $\text{KCl}$  molecule if there were opposite charges of one fundamental unit located at each nucleus. Calculate the percentage ionic character of  $\text{KCl}$ .  
[IIT 1993]

**Solution** Dipole moment

$$\mu = e \times d \text{ coulombs meter}$$

$$\text{For KCl} \quad d = 2.6 \times 10^{-10} \text{ m}$$

For complete separation of unit charge (electronic charge),

$$e = 1.602 \times 10^{-19} \text{ C}$$

Hence

$$\mu = 1.602 \times 10^{-19} \times 2.6 \times 10^{-10}$$

$$= 4.1652 \times 10^{-29} \text{ cm}$$

$$\mu (\text{KCl}) = 3.336 \times 10^{-29} \text{ cm}$$

Percent ionic character of  $\text{KCl}$

$$= \frac{3.336 \times 10^{-29}}{4.1652 \times 10^{-29}} \times 100$$

$$= 80.09 \%$$

5. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition  $n = 4$  to  $n = 2$  of  $\text{He}^+$  spectrum?

[IIT 1993]

**Solution** For  $\text{He}^+$ ,

$$\frac{1}{\lambda} = R_H Z^2 \left( \frac{1}{2^2} - \frac{1}{4^2} \right).$$

For H,

$$\frac{1}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right).$$

Since  $\lambda$  is same

$$Z^2 [1/2^2 - 1/4^2] = [1/n_1^2 - 1/n_2^2]$$

$$Z = 2$$

$$[1/1^2 - 1/2^2] = [1/n_1^2 - 1/n_2^2]$$

$$n = 1 \text{ and } n = 2.$$

6. Find the number of waves made by a Bohr electron in one complete revolution in the 3<sup>rd</sup> orbit.

[IIT 1994]

**Solution** Velocity of the electron in 3<sup>rd</sup> orbit =  $\frac{3h}{2\pi mr}$

Here  $m$  = mass of electron

$r$  = radius of 3<sup>rd</sup> orbit

According to de Broglie equation

$$\lambda = \frac{h}{mv} = \frac{h}{m} \times \frac{2\pi mr}{3h} = \frac{2\pi r}{3}$$

$$\text{Number of waves} = \frac{2\pi r}{\lambda}$$

$$= \frac{2\pi r}{2\pi r} \times 3 = 3$$

7. A bulb emits light of  $\lambda$  4500 Å. The bulb is rated as 150 watt and 8 per cent of the energy is emitted as light. How many photons are emitted by the bulb per second?

[IIT 1995]

**Solution** Energy of one photon =  $\frac{hc}{\lambda}$

$$= \frac{6.625 \times 10^{-34} \times 3 \times 10^8 \text{ J}}{4500 \times 10^{-10}}$$

$$= 4.42 \times 10^{-19} \text{ J}$$

$$\text{Energy emitted by the bulb} = 150 \times \frac{8}{100} \text{ J}$$

$$n \times 4.42 \times 10^{-19} = 150 \times \frac{8}{100}$$

$$n = 27.2 \times 10^{18}$$

8. Iodine molecule dissociates into atoms after absorbing light of 4500 Å. If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms. (bond energy of  $I_2 = 240 \text{ kJ mol}^{-1}$ ).

[IIT 1995]

**Solution** Energy used for breaking up  $I_2$  molecule

$$= \text{bond energy of } I_2 = 240 \text{ kJ mol}^{-1}$$

$$= 240 \times 10^3 \text{ J mol}^{-1}$$

$$= \frac{240 \times 10^3}{6.023 \times 10^{23}} \text{ J molecule}^{-1}$$

$$= 3.984 \times 10^{-19} \text{ J molecule}^{-1}$$

$$\text{Energy absorbed by } I_2 \text{ molecule} = \frac{hc}{\lambda}$$

$$= \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1}}{4500 \times 10^{10} \text{ m}}$$

$$= 4.417 \times 10^{-19} \text{ J}$$

Energy used in imparting kinetic energy to one  $I_2$  molecule

$$1. = 4.417 \times 10^{-19} - 3.984 \times 10^{-19} \text{ J} = 4.33 \times 10^{-20} \text{ J}$$

Energy used in imparting kinetic energy to each iodine atom

$$= \frac{4.33 \times 10^{-20}}{2} = 2.165 \times 10^{-20} \text{ J}$$

9. Consider the hydrogen atom to be a proton embedded in a cavity of radius  $a_0$  (Bohr's radius), whose charge is neutralized by the addition of an electron to the cavity in vacuum, infinitely slowly.

(a) Estimate the average of total energy of an electron in its ground state in a hydrogen atom as the work done in the above neutralization process. Also if the magnitude of the average kinetic energy is half the magnitude of the average potential energy, find the average potential energy.

(b) Also derive the wavelength of the electron when it is  $a_0$  from the proton. How does this compare with the wavelength of an electron in the ground state Bohr's orbit?

[IIT 1996]

**Solution** (a) Work done in bringing the electron from  $a$  to  $a_0$  is given by

$$W = -\frac{e^2}{4 \pi \epsilon_0 a_0^2}$$

It is equal to total energy. As in the problem the kinetic energy at this condition is assumed to be zero so it will be equal to potential energy.

that is, Total energy = P.E. + K.E.

$$= \text{P.E.} = -\frac{e^2}{4 \pi \epsilon_0 a_0}$$

Now as the electron is to be captured by the proton to form ground state H-atom. There must be kinetic energy also which is half of the potential energy assume in this problem

$$\text{that is, } (\frac{e^2}{8 \pi \epsilon_0 a_0})$$

Hence total energy = P.E. + K. E

$$= -\frac{e^2}{4 \pi \epsilon_0 a_0} + \frac{e^2}{8 \pi \epsilon_0 a_0}$$

$$= -\frac{e^2}{8 \pi \epsilon_0 a_0}$$

$$(b) \text{ Wavelength } (\lambda) = \frac{h}{p} = \frac{h}{mv} \quad \dots(i)$$

$$\text{As K.E.} = \frac{1}{2} mv^2 \quad \dots(ii)$$

$$v = \frac{m}{p} \quad \dots(iii)$$

From these equation (i), (ii) and (iii)

$$\lambda = \frac{h}{\sqrt{(2 m \cdot \text{K.E.})}}$$

As K.E. = 0 at this situation, so  $\lambda = \infty$

When electron is at a distance  $a_0$  in Bohr's orbit of H atom wave length is as follows:

$$\lambda = \frac{h}{\sqrt{(2 m \cdot \text{K.E.})}}$$

$$= \frac{h}{\sqrt{(2me^2/8 \pi \epsilon_0 a_0)}}$$

$$\lambda = \frac{h}{\sqrt{(e^2 m/4 \pi \epsilon_0 a_0)}}$$

10. Calculate the wavelength for the shortest wave length transition in the Balmer series of atomic hydrogen.

[IIT 1996]

**Solution**  $\bar{V} = \frac{1}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ .

$$= 109677 (1/4 - 0) = \frac{109677}{4}$$

$$= 27419.25 \text{ cm}^{-1}$$

### 3.28 ■ Atomic Structure

11. A compound of vanadium has a magnetic moment of 1.73 B.M. Work out the electronic configuration of the vanadium ion in the compound.

[IIT 1997]

**Solution** Magnetic moment = 1.73 B.M =  $\sqrt{N(N+2)}$

Here N = number of unpaired electrons

$$N = 1$$

It means that in the compound vanadium ion must have one unpaired electrons.

$$_{23}V = 1s^2, 2s^2 2p^6, 3s^2 3p^6 4s^2 3d^3$$

$$V^{+4} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1$$

12. An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to  $1.54 \text{ \AA}$ .

[IIT 1997]

**Solution**  $\frac{1}{2} m u^2 = e V$

$$\lambda = \frac{h}{mu}$$

$$u = \frac{h}{m\lambda} \text{ or } u^2 = \frac{h^2}{m^2 \lambda^2}$$

$$\frac{1}{2} m \times \frac{h^2}{m^2 \lambda^2} = eV$$

$$V = \frac{1}{2} m \times \frac{h^2}{m^2 \lambda^2 \times e}$$

$$V = \frac{1}{2} \times \frac{h^2}{m \lambda^2 e}$$

$$= \frac{1}{2} \times \frac{(6.62 \times 10^{-34})^2}{9.108 \times 10^{-31} \cdot (1.54 \times 10^{-10})^2 \times 1.602 \times 10^{-19}}$$

$$= 63.3 \text{ volt}$$

13. State the number of protons, neutrons and electrons in  $C^{12}$  and  $C^{14}$ .

[IIT 1997]

**Solution** The atomic number of  $C^{12}$  is 6. So in it number of electrons = 6.

$$\text{Number of protons} = 6$$

$$\text{Number of neutrons} = 12 - 6 = 6$$

$$\text{In}_6C^{14}$$

$$\text{Number of electrons} = 6$$

$$\text{Number of protons} = 6$$

$$\text{Number of neutrons} = 14 - 6$$

14. Calculate the energy required to excite one litre of hydrogen gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H – H bond is 436 kJ mol<sup>-1</sup>. Also calculate the minimum frequency of photon to break this bond.

[IIT 2000]

**Solution** As  $n = \frac{PV}{RT}$

So mole of  $H_2$  present in one litre (n) =  $PV/RT$

$$= \frac{1 \times 1}{0.0821 \times 298} = 0.0409$$

Hence energy needed to break H – H bonds in 0.0409 mole of  $H_2$

$$= 0.0409 \times 436 = 17.83 \text{ kJ}$$

Now energy needed to excite one H atom from first to second energy level

$$= 13.6 \left(1 - \frac{1}{4}\right) \text{ eV}$$

$$= 10.2 \text{ eV}$$

$$= 10.2 \times 1.6 \times 10^{-19} \text{ J}$$

So energy needed to excite  $0.0409 \times 2 \times 6.02 \times 10^{23}$  atoms of H

$$= 10.2 \times 1.6 \times 10^{-19} \times 0.0409 \times 2 \times 6.02 \times 10^3 \text{ J}$$

$$= 80.36 \text{ kJ}$$

that is, total energy needed =  $17.83 + 80.36$

$$= 98.19 \text{ kJ}$$

Now energy required to break (H – H) bond

$$= \frac{436 \times 10^3}{6.023 \times 10^{23}} \text{ Joule}$$

Using  $E = hv$

$$\text{that is, } \frac{436 \times 10^3}{6.023 \times 10^{23}} = 6.626 \times 10^{-34} \times v.$$

On solving

$$v = 10.93 \times 10^{14} \text{ sec}^{-1} \text{ or Hz}$$

15. Wavelength of high energy transition of H-atoms is 91.2 nm. Calculate the corresponding wavelength of  $He^+$ .

[IIT 2003]

**Solution** For H-atom

$$\frac{1}{\lambda_1} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \dots\dots(1)$$

For  $\text{He}^+$  ion :

$$\frac{1}{\lambda_2} = R_H Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \dots\dots(2)$$

By (1) and (2),

$$\frac{\lambda_2}{\lambda_1} = \frac{1}{Z^2}$$

$$\text{or } \lambda_{\text{He}^+} = \lambda_H \times \frac{1}{Z^2} = 91.2 \times \frac{1}{2^2} = 22.8 \text{ nm}$$

16. The wave function of 2s electron is given by

$$\psi^{2s} = \frac{1}{4\sqrt{2\pi}} (1/a_0)^{3/2} \left( 2 - \frac{r}{a_0} \right) e^{-r/a_0}$$

It has a node at  $r = r_0$ , find relation between  $r_0$  and  $a_0$ .

[HIT 2004]

**Solution** The probability of finding of 2s electron at a point is given as follows:

$$\psi_{2s}^2 = \frac{1}{32\pi} (1/a_0)^3 \left( 2 - \frac{r}{a_0} \right)^2 e^{-2r/a_0}$$

As node is the point at which probability of finding an electron is zero

that is,  $\psi_{2s}^2 = \text{zero}$

It is possible when  $r = r_0$

$$\text{that is, } \frac{1}{32\pi} (1/a_0)^3 \left( 2 - \frac{r_0}{a_0} \right)^2 e^{-2r_0/a_0} = 0$$

$$\text{On solving } 2 - \frac{r_0}{a_0} = 0$$

$$r_0 = 2 a_0$$

17. Find the wavelength for 100 g particle moving with velocity  $100 \text{ ms}^{-1}$ .

[HIT 2004]

**Solution** According to de Broglie equation:

$$\begin{aligned} \lambda &= \frac{h}{mv} \\ &= \frac{6.626 \times 10^{-34} \text{ J.s}}{(100 \times 10^{-3} \text{ kg}) \times 100 \text{ ms}^{-1}} \\ &= 6.626 \times 10^{-35} \text{ m} \end{aligned}$$

18. Find the velocity ( $\text{ms}^{-1}$ ) of electron in first Bohr's orbit of radius  $a_0$ . Also find the de Broglie's

wavelength (in m). Calculate the orbital angular momentum of 2p orbital of hydrogen atom in units of  $\hbar/2\pi$ .

[IIT 2005]

**Solution** For hydrogen atom,  $Z = 1, n = 1$

$$v = 2.18 \times 10^6 \times \frac{Z}{n} \text{ ms}^{-1} = 2.18 \times 10^6 \text{ ms}^{-1}$$

de Broglie wavelength

$$\begin{aligned} \lambda &= \frac{h}{mv} = \frac{6.26 \times 10^{-34}}{9.1 \times 10^{-31} \times 2.18 \times 10^6} \\ &= 3.34 \times 10^{-10} \text{ m} = 3.3 \text{ \AA} \end{aligned}$$

For 2p,  $l = 1$

Orbital angular momentum ( $mvrl$ )

$$= \sqrt{l(l+1)} \frac{h}{2\pi} = \sqrt{2} \frac{h}{2\pi}$$

19. What is the angular momentum of an electron in Bohr's hydrogen atom whose energy is  $-3.4 \text{ eV}$ ?

**Solution** As  $E = -\frac{13.6}{n^2}$

$$-3.4 = -\frac{13.6}{n^2}$$

$$n = 2$$

The angular momentum quantization gives

$$L = mvrl = \frac{nh}{2\pi}$$

On substituting  $n = 2$ , we have

$$L = \frac{2h}{2\pi} = \frac{h}{\pi}$$

20. Consider a hydrogen like atom whose energy in  $n$ th excited state is given by

$$E_n = -\frac{13.6 Z^2}{n^2}$$

When this excited atom makes a transition from excited state to ground state, most energetic photons have energy  $E_{\max} = 52.554 \text{ eV}$  and least energetic photons have energy  $E_{\min} = 1.224 \text{ eV}$ . Find the atomic number of atom and the state of excitation.

**Solution** Maximum energy is liberated for transition

$$E_n \rightarrow 1 \text{ and minimum energy for } E_n \rightarrow E_{n-1}$$

$$\frac{E_1}{n^2} - E_1 = 52.224 \text{ eV} \quad \dots\dots(i)$$

### 3.30 ■ Atomic Structure

$$\frac{E_1}{n^2} - \frac{E_1}{(n-1)^2} = 1.224 \text{ eV} \quad \dots \text{(ii)}$$

On solving the equations, we get

$$E_1 = -54.4 \text{ eV}$$

$$n = 5$$

$$E_1 = -\frac{13.6 Z^2}{1^2} = -54.4 \text{ eV}$$

$$Z = 2$$

Therefore the gas is helium, originally excited to  $n = 5$  energy state.

- 21.** An  $\alpha$ -particle and a proton are fired through the same magnetic fields which is perpendicular to their velocity vectors. The  $\alpha$ -particle and the proton move such that radius of curvature of their path is same. Calculate the ratio of their de Broglie wavelengths.

**Solution** Magnetic force experienced by a charged particle in magnetic field is given by,

$$F_B = q \vec{v} \times \vec{B} = qvB \sin \theta$$

$$\text{As } \theta = 0$$

$$\text{So } F_B = q v B$$

$$Bqv = \frac{mv^2}{r}$$

$$\text{or } mv = qBr$$

The de Broglie wavelength

$$\lambda = \frac{h}{mv} = \frac{h}{qBr} .$$

$$\frac{\lambda (\alpha\text{-particle})}{\lambda (\text{proton})} = \frac{q_p r_p}{q_a r_a}$$

$$\text{As } \frac{r_a}{r_p} = 1 \text{ and } \frac{q_a}{q_p} = 2$$

$$\text{So } \frac{\lambda_a}{\lambda_p} = \frac{1}{2}$$

- 22.** Calculate the ratio of de Broglie wavelength of a proton and an  $\alpha$ -particle which have been accelerated through same potential difference.

**Solution** Kinetic energy gained by a charge 'q' after being accelerated through a potential difference V volt.

$$qV = \frac{1}{2} mv^2$$

$$v = \sqrt{2qV/m}$$

$$mv = \sqrt{2mqV}$$

According to de Broglie wavelength

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2mqV}}$$

$$\frac{\lambda_p}{\lambda_a} = \frac{\sqrt{(m_a q_a V_a)}}{\sqrt{m_p q_p V_p}}$$

On Putting  $V_a = V_p$  we get

$$\frac{\lambda_p}{\lambda_a} = \frac{\sqrt{(4 \times 2)}}{\sqrt{(1 \times 1)}} = 2\sqrt{2}$$

- 23.** Calculate the wavelength for an  $n = 2$  to  $n = 1$  transition in molybdenum ( $Z = 42$ ). What is the energy of such a photon?

**Solution** According to Bohr formula  $Z^2$  is replaced by  $(Z-1)^2 = (41)^2$ . For  $n = 2$  to  $n = 1$  transition in hydrogen ( $Z = 1$ )

$$\lambda \propto \frac{1}{(Z-1)^2}$$

$$\lambda = \frac{(1.22 \times 10^{-7})}{(41)^2} = 0.073 \text{ nm}$$

It is close to the measured value of 0.071 nm. Each of these photons would have energy (in eV) of:

$$E = hf = \frac{hc}{\lambda}$$

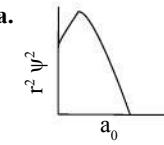
$$= \frac{6.63 \times 10^{-34} \times 3.00 \times 10^8}{7.3 \times 10^{-11} \times 1.60 \times 10^{-19}} = 17 \text{ KeV}$$

## MULTIPLE-CHOICE QUESTIONS

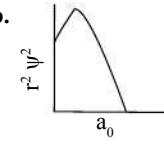
### Straight Objective Type Questions (Single Choice only)

1. The quantum number 'm' of a free gaseous atom is associated with
  - the effective volume of the orbital
  - the shape of the orbital
  - the spatial orientation of the orbital
  - the energy of the orbital in the absence of a magnetic field
2. The angular momentum ( $L$ ) of an electron in a Bohr orbit is given as
  - $L = nh/2\pi$
  - $b. \sqrt{l(l+1) h/2\pi}$
  - $c. L = mg/2\pi$
  - $d. L = h/4\pi$
3. When the azimuthal quantum number has the value of 2, the number of orbitals possible are
  - 0
  - 4
  - 1
  - 5
4. For a d-electron, the orbital angular momentum is
  - $\sqrt{6}\hbar$
  - $\sqrt{2}\hbar$
  - $\hbar$
  - $2\hbar$
5. The ratio of kinetic energy and potential energy of an electron in a Bohr orbit of a hydrogen like species is
  - 1
  - +1
  - $-\frac{1}{2}$
  - $+\frac{1}{2}$
6. In which of the following sets do all species have the same number of electrons?
  - O, O<sup>2-</sup>, O<sup>2+</sup>
  - Mg<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>
  - Br<sup>-</sup>, Kr, Sr<sup>2+</sup>
  - C, N<sup>3-</sup>, O<sup>2-</sup>
7. Of the following, which has the shortest de Broglie wavelength?
  - A nitrogen molecule moving at a velocity of 4000 mph.
  - A nitrogen molecule moving at a velocity of 1100 mph
  - A helium nucleus moving at a velocity of 1200 mph
  - An airplane moving at a velocity of 200 mph
8. Gaseous metal ion M<sup>2+</sup> has 5 unpaired electrons. What is its atomic number?
  - 25
  - 26
  - 27
  - 28

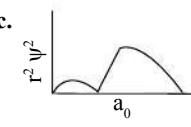
9. The electronic configuration  $1s^2, 2s^2, 2p^6, 3s^1, 3p^1$  is correctly described by
  - the excited state of Mg<sup>+</sup>
  - the excited state of Na<sup>+</sup>
  - the excited state of Mg
  - the excited state of Al.
10. The orbital angular momentum of an electron in 2s orbital is
  - $+\frac{1}{2} \frac{\hbar}{2\pi}$
  - zero
  - $\frac{\hbar}{2\pi}$
  - $\sqrt{2} \frac{\hbar}{2\pi}$
11. Which of the following radial distribution graphs correspond to  $l = 2$  for Hydrogen atom:
 



a.



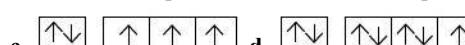
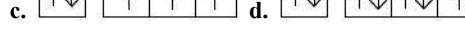
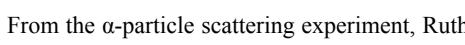
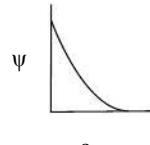
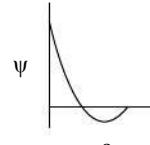
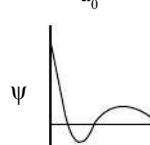
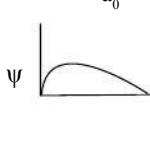
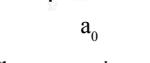
b.

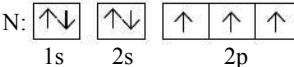


c.

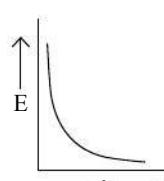
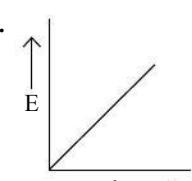
d. Both (a) and (b)
12. In which of the following pairs are both the ions coloured in aqueous solution?  
 (At. no. Sc = 21, Ti = 22, Ni = 28, Cu = 29, Co = 27)
  - Sc<sup>3+</sup>, Co<sup>2+</sup>
  - Ni<sup>2+</sup>, Cu<sup>+</sup>
  - Ni<sup>2+</sup>, Ti<sup>3+</sup>
  - Sc<sup>3+</sup>, Ti<sup>3+</sup>
13. Rutherford's  $\alpha$ -particles scattering experiment led to the conclusion that:
  - Atoms are electrically neutral
  - Mass and energy are related
  - Mass and positive charge of an atom are concentrated in the nucleus
  - Neutrons are present in the nucleus
14. Each p-orbital and each d-orbital has lobes respectively as
  - 2, 4
  - 1, 2
  - 2, 2
  - 1, 1
15. The mass of an electron is m. Its charge is e and it is accelerated from rest through a potential difference V. The velocity acquired by the electron will be

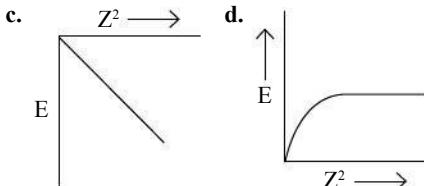
### 3.32 ■ Atomic Structure

- a.  $\sqrt{V/m}$       b.  $\sqrt{eV/m}$   
 c.  $\sqrt{2eV/m}$       d. none
16. For an orbital, a node is  
 a. A surface inside which there is a 90% chance of finding the electron.  
 b. The mid point of the orbital  
 c. A surface where there is no chance of finding the electron  
 d. A surface where there is a maximum probability of finding the electron.
17. In the photoelectric effect, in order for an electron to be released from the surface of a clean metal, which one of the following conditions must exist?  
 a. The kinetic energy of photons striking the metal's surface must be less than that of the emitted electrons  
 b. The kinetic energy of photons striking the metal's surface must be greater than or equal to that of the emitted electrons plus the binding energy holding the electron in the metal  
 c. The metal must have a low temperature  
 d. The kinetic energy of photons striking the metal's surface must equal that of the emitted electron
18. Which of the following transitions will have minimum wavelength?  
 a.  $n_4 \rightarrow n_2$       b.  $n_4 \rightarrow n_1$   
 c.  $n_2 \rightarrow n_1$       d.  $n_3 \rightarrow n_1$
19. Which of the following relates to photons both as wave motion and as a stream of particles?  
 a. interference      b.  $E = mc^2$   
 c. diffraction      d.  $E = hv$
20. A metal surface is exposed to solar radiations  
 a. The emitted electrons have zero energy  
 b. The emitted electrons have energy equal to energy of photons of incident light  
 c. The emitted electrons have energy less than the maximum value of energy depending upon intensity of incident radiations.  
 d. The emitted electrons have energy less than a maximum value of energy depending upon the frequency of the incident radiation.
21. The ionization energy of hydrogen atom is 13.6 eV. What will be the ionization energy of  $\text{He}^+$ ?  
 a. 13.6 eV      b. 54.4 eV  
 c. 122.4 eV      d. zero
22. The H-spectrum shows  
 a. Polarization  
 b. Presence of quantized energy levels  
 c. Heisenberg's uncertainty principle  
 d. Diffraction
23. Which of the following represents the correct set up of the four quantum number of 4s electron  
 a. 4, 1, 0,  $+\frac{1}{2}$       b. 4, 1,  $-1, -\frac{1}{2}$   
 c. 4, 2, 1,  $+\frac{1}{2}$       d. 4, 0, 0,  $\frac{1}{2}$
24. The orbital diagram in which the Aufbau principle is violated is
- |                                     |                                     |                                     |    |
|-------------------------------------|-------------------------------------|-------------------------------------|----|
| 2s                                  | 2p                                  | 2s                                  | 2p |
| <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> |    |
- a. 
- |                                     |                          |                          |                          |
|-------------------------------------|--------------------------|--------------------------|--------------------------|
| 2s                                  | 2p                       | 2s                       | 2p                       |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |
- b. 
- |                                     |                          |                          |                          |
|-------------------------------------|--------------------------|--------------------------|--------------------------|
| 2s                                  | 2p                       | 2s                       | 2p                       |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |
- c. 
- |                                     |                          |                          |                          |
|-------------------------------------|--------------------------|--------------------------|--------------------------|
| 2s                                  | 2p                       | 2s                       | 2p                       |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |
- d. 
25. From the  $\alpha$ -particle scattering experiment, Rutherford concluded that:  
 a. The radius of the nucleus is less than  $10^{-12}$  m  
 b.  $\alpha$ -particles can approach within a distance of the order of  $10^{-14}$  m of the nucleus  
 c. The positively charged parts of the atom move with extremely high velocities  
 d. Scattering does not follow Coulomb's law.
26. Electromagnetic radiation with maximum wavelength is  
 a. radiowave      b. X-ray  
 c. infrared      d. ultraviolet
27. Which order of energies of orbitals is correct in a many electron atom?  
 a.  $3d < 2s$       b.  $2s = 2p$   
 c.  $4s > 5s$       d.  $3s < 3p$
28. The subshell designations follows the alphabet after 'f'. What is the first shell in which an 'h' orbital would be allowed?  
 a. Fourth      b. Fifth  
 c. Sixth      d. Seventh
29. The graph representing two nodes is
- |                                                                                        |                                                                                          |
|----------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| a.  | b.  |
|----------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
- a. 
- |                                                                                          |                                                                                        |
|------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|
| c.  | d.  |
|------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|
30. When potassium metal is exposed to violet light  
 a. there is no effect  
 b. ejection of electron takes place

- c. the absorption of electrons takes place  
d. ejection of some potassium atoms occurs
- 31.** Which of the following orbitals can have more than one nodal plane?
- a. 1s                    b. 2s  
c. 2p                    d. 3d
- 32.** The radius of an atomic nucleus is of the order of
- a.  $10^{-8}$  cm            b.  $10^{-13}$  cm  
c.  $10^{-10}$  cm            d.  $10^{-15}$  cm
- 33.** Find the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.
- a. 6.9 BM              b. 5.9 BM  
c. 4.9 BM              d. 3.0 BM
- 34.** Bohr model can explain
- a. the solar spectrum  
b. the spectrum of hydrogen molecule  
c. the spectrum of hydrogen atom only  
d. spectrum of an atom or ion containing one electron only
- 35.** An electron is moving in Bohr's fourth orbit. Its deBroglie wavelength is  $\lambda$ . What is the circumference of the fourth orbit?
- a.  $2\lambda$                 b.  $2/\lambda$   
c.  $3\lambda$                 d.  $4\lambda$
- 36.** Which one of the following grouping represents a collection of isoelectronic species? (At numbers Cs-55, Br -35)
- a.  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$   
b.  $\text{N}^3-$ ,  $\text{F}^-$ ,  $\text{Na}^+$   
c.  $\text{Be}$ ,  $\text{Al}^{3+}$ ,  $\text{Cl}^-$   
d.  $\text{Ca}^{2+}$ ,  $\text{Cs}^+$ ,  $\text{Br}$
- 37.** Which of the following represent electron configuration that violate the Pauli exclusion principle?
- (I)  $[\text{Ne}] 3s^1 3p^5$   
(II)  $[\text{Kr}] 4d^{12} 5s^2 5p^3$   
(III)  $[\text{Ar}] 3d^{10} 4s^2 4p^2$
- a. Only (II)  
b. Only (I)  
c. Both (I) and (III)  
d. Both (II) and (III)
- 38.** Which best describes the emission spectra of atomic hydrogen?
- a. A discrete series of lines of equal intensity and equally spaced with respect to wavelength  
b. A series of only four lines
- c. A continuous emission of radiation of all frequencies  
d. Several discrete series of lines with both intensity and spacing between lines decreasing as the wave number increases within each series
- 39.** Which electronic level would allow the hydrogen atom to absorb a photon but not to emit a photon?
- a. 1s                    b. 2s  
c. 2p                    d. 3s
- 40.** In the electronic configuration given below which rule is violated?
- N:   
1s          2s          2p
- a. Aufbau rule  
b. Pauli's exclusion principle  
c. Hund's rule  
d. No violation of any of these rules
- 41.** The number of d-electrons in Ni (atomic number = 28) is equal to that of the
- a. d-electrons in  $\text{Ni}^{2+}$   
b. Total electrons in N (atomic number = 7)  
c. s and p-electrons in  $\text{F}^-$   
d. p-electrons in Ar (atomic number = 18)
- 42.** In a multi-electron atom, which of the following orbitals described by the three quantum numbers will have the same energy in the absence of magnetic field and electric fields?
- a.  $n = 1, l = 0, m = 0$   
b.  $n = 2, l = 0, m = 0$   
c.  $n = 3, l = 1, m = 1$   
d.  $n = 3, l = 2, m = 1$   
e.  $n = 3, l = 2, m = 0$
- a. b and c              b. d and e  
c. c and d              d. a and b
- Ans b.
- 43.** Correct set of four quantum numbers for the valence (outermost) electron of rubidium ( $Z = 37$ ) is
- a.  $5, 0, 0, \pm \frac{1}{2}$             b.  $6, 0, 0, + \frac{1}{2}$   
c.  $5, 1, 1, \pm \frac{1}{2}$             d.  $5, 1, 0, \pm \frac{1}{2}$
- 44.** If  $n = 3, l = 0, m = 0$ , then atomic number is
- a. 12, 14                b. 11, 13  
c. 11, 12                d. 13, 14
- 45.** How many lines in the spectrum will be observed when electrons return from 7th shell to 2nd shell?
- a. 10                    b. 15  
c. 21                    d. 30

### 3.34 ■ Atomic Structure

- 46.** The increasing order (lowest first) for the values of  $e/m$  (charge/mass) for electron (e), proton (p), neutron (n) and alpha particle (a) is:
- n, p, a, e
  - n, p, e, a
  - n, a, p, e
  - e, p, n, a
- 47.** For a hydrogen atom, which electronic transition would result in the emission of a photon with the highest energy?
- $5f \rightarrow 3d$
  - $4p \rightarrow 2s$
  - $3p \rightarrow 6d$
  - $2s \rightarrow 3p$
- 48.** The specific charge for positive rays is much less than the specific charge for cathode rays. This is because
- Charge on positive rays is less
  - Positive rays are positive charged
  - Experimental method for determination is wrong
  - Positive rays comprise ionized atoms whose mass is much higher
- 49.** In iron, which of the following electrons, characterized by the four quantum numbers, has the lowest energy?
- $n = 3, l = 2, m_l = 1, m_s = -\frac{1}{2}$
  - $n = 3, l = 2, m_l = 0, m_s = +\frac{1}{2}$
  - $n = 3, l = 1, m_l = 0, m_s = +\frac{1}{2}$
  - $n = 4, l = 0, m_l = 0, m_s = +\frac{1}{2}$
- 50.** Rutherford's scattering experiment is related to the size of the
- atom
  - nucleus
  - neutron
  - electron
- 51.** Wave function of an orbital is given below in the variation or w.r.t. distance from nucleus.
- 
- It may be the graphical representation of
- 1s
  - 2s
  - 2p
  - 3s
- 52.** If the electron of a hydrogen atom is present in the first orbit, the total energy of the electron is .....
- $-e^2/2r$
  - $-e^2/r$
  - $-e^2/2r^2$
  - $-e^2/2r^2$
- 53.** The principal quantum number of an atom is related to the
- orientation of the orbital in space
  - spin angular momentum
- c.** orbital angular momentum
- d.** size of the orbital
- 54.** Name the ions indicated by the following electronic configurations:
1.  $\text{-----} \begin{array}{|c|c|c|c|c|c|} \hline & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline \end{array} \quad 3d$
2.  $\text{-----} \begin{array}{|c|c|c|} \hline & \uparrow & \uparrow & \uparrow \\ \hline \end{array} \quad 4d$
- $\text{Ni}^{2+}, \text{Br}^-$
  - $\text{Zn}^{2+}, \text{Rb}^{2+}$
  - $\text{Cu}^{2+}, \text{Se}^{2-}$
  - $\text{Co}^{3+}, \text{Rb}^+$
- 55.** Which of the following sets of quantum numbers represents the electron of the lowest energy?
- $n = 2, l = 0, m = 0, s = -\frac{1}{2}$
  - $n = 2, l = 1, m = 0, s = +\frac{1}{2}$
  - $n = 4, l = 2, m = 0, s = +\frac{1}{2}$
  - $n = 4, l = 0, m = 0, s = -\frac{1}{2}$
- 56.** The orbital angular momentum for an electron revolving in an orbit is given by  $\sqrt{l(l+1)} h/2\pi$ . This momentum for an s-electron will be given by:
- $+\frac{1}{2}h/2\pi$
  - zero
  - $h/2\pi$
  - $\sqrt{2}h/2\pi$
- 57.** Any p-orbital can accommodate upto
- six electrons
  - four electrons
  - two electrons with opposite spins
  - two electrons with parallel spins
- 58.** The energy of an electron moving in nth Bohr's orbit of an element is given by
- $$E_n = \frac{13.6}{n^2} Z^2 \text{ eV /atom}$$
- Here  $Z$  = atomic number
- The graph of  $E$  vs  $Z^2$  will be:
- a. 
- b. 



59. The fourth electron of Be atom will have quantum numbers as
- $1, 0, 0, \frac{1}{2}$
  - $2, 0, 0, -\frac{1}{2}$
  - $2, 1, 0, +\frac{1}{2}$
  - $1, 1, 1, +\frac{1}{2}$
60. Which of the following electronic configuration does not follow the Pauli's exclusion principle?
- $1s^2 2s^2 2p^4$
  - $1s^2 2s^2 2p^6 3s^2$
  - $1s^2 2s^2$
  - $1s^2 2s^2 2p^6 3s^3$
61. In which of the following, pair both the ions have magnetic moment 2.83 B.M. respectively?
- $Fe^{2+}, Mn^{2+}$
  - $Fe^{3+}, Mn^{2+}$
  - $Mn^{2+}, Cr^{3+}$
  - $Mn^{2+}, V^{4+}$
62. Uncertainty in position of a particle of 25 g in space is  $10^{-5}$  m. Hence uncertainty in velocity ( $m s^{-1}$ ) is (Planck's constant  $h = 6.6 \times 10^{-34}$  Js)
- $2.1 \times 10^{-28}$
  - $2.1 \times 10^{-34}$
  - $0.5 \times 10^{-34}$
  - $5.0 \times 10^{-24}$
63. Which of the following options represent the correct graph for photoelectrons?
- a.
- b.
- c. Both of the above
- d. None of the above
64. Which of the following ions has the maximum magnetic moment?
- $Mn^{2+}$
  - $Fe^{2+}$
  - $Ti^{2+}$
  - $Cr^{2+}$
65. The de Broglie wavelength of a tennis ball of mass 60 g moving with a velocity of 10 meters per second is approximately:  
(Planck's constant  $h = 6.63 \times 10^{-31}$  Js)

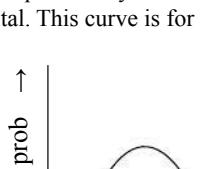
- $10^{-33}$  m
  - $10^{-31}$  meter
  - $10^{-16}$  m
  - $10^{-25}$  m
66. The number of d-electrons retained in  $Fe^{2+}$  (At. number of Fe = 26) ions is
- 3
  - 4
  - 5
  - 6
67. Which one of the following sets of ions represents the collection of isoelectronic species?
- $K^+, Ca^{2+}, Sc^{3+}, Cl^-$
  - $Na^+, Ca^{2+}, Sc^{3+}, F^-$
  - $K^+, Cl^-, Mg^{2+}, Sc^{3+}$
  - $Na^+, Mg^{2+}, Al^{3+}, Cl^-$
68. Transition of an electron from  $n = 3$  level to  $n = 1$  level results in:
- Band spectrum
  - IR spectrum
  - Emission spectrum
  - X-ray spectrum
69. For a particular orbital, as one goes away from the nucleus along the Z-axis, the probability density decreases to zero, then increases, and finally decreases without increasing a second time. This is consistent with a
- $2s$  or a  $2p_z$  orbital
  - $2s$  orbital
  - $3s$ -orbital
  - $2p_z$  orbital
70. Of the following sets which one does not contain isoelectronic species?
- $PO_4^{3-}, SO_4^{2-}, ClO_4^-$
  - $CN^-, N_2, C_2^{2-}$
  - $SO_3^{2-}, CO_3^{2-}, NO_3^-$
  - $BO_3^{3-}, CO_3^{2-}, NO_3^-$
71. The orbital diagram in which the Pauli's exclusion principle is violated is
- a.
- b.
- c.
- d.
72. According to Bohr's theory, the angular momentum of an electron in 5th orbit is
- $25 h/\pi$
  - $1.0 h/\pi$
  - $10 h/\pi$
  - $2.5 h/\pi$
73. If the electronic structure of oxygen atom is  
 $\leftarrow 2p \rightarrow$   
written as  $1s^2, 2s^2, \boxed{\uparrow \downarrow} \boxed{\uparrow \downarrow} \boxed{\phantom{\uparrow \downarrow}}$  it would violate:

### 3.36 ■ Atomic Structure

- a. Hund's rule  
 b. Pauli's exclusion principle  
 c. Both Hund's and Pauli's principles  
 d. None of these

74. Passing an electrical charge through argon gas contained in a partially evacuated vessel yields which of the following?  
 a. A line spectrum  
 b. A continuous spectrum  
 c. No visible change  
 d. White light

75. Here radial probability distribution curve is shown for s-orbital. This curve is for



a. 3s  
 b. 1s  
 c. 2s  
 d. All of these

79. A monoenergetic electron beam with a de Broglie wavelength of 'P' Å is accelerated till its wavelength is halved. By what factor will its kinetic energy change?  
 a. 2  
 b.  $\frac{1}{2}$   
 c. 4  
 d. Remains same

80. The first emission line in the atomic spectrum of hydrogen in the Balmer series appears at:  
 a.  $\frac{3R}{4}$  cm<sup>-1</sup>  
 b.  $\frac{5R}{36}$  cm<sup>-1</sup>  
 c.  $\frac{36}{5R}$  cm<sup>-1</sup>  
 d.  $\frac{7R}{36}$  cm<sup>-1</sup>

81. The isoelectronic pair is:  
 a.  $\text{ClO}_2^-$ ,  $\text{ClF}_2^+$   
 b.  $\text{IF}_2^+$ ,  $\text{I}_3^-$   
 c.  $\text{Cl}_2\text{O}_3$ ,  $\text{ICl}_2^-$   
 d.  $\text{ICl}_2^-$ ,  $\text{ClO}_2$

82. If Aufbau rule is not followed then percent change in total  $(n + l)$  value for unpaired electrons in  $^{25}\text{Mn}$  is:  
 a. 60  
 b. 50  
 c. 40  
 d. 30

83. A photon of wavelength 300 nm is absorbed by a gas and then re-emitted as two photons. One photon is red with wavelength of 760 nm. The wave number of the second photon will be  
 a.  $2.20 \times 10^7 \text{ m}^{-1}$   
 b.  $2.02 \times 10^6 \text{ m}^{-1}$

## Brainteasers Objective Type Questions (Single choice only)

76. The number of waves made by a Bohr electron in an orbit of maximum magnetic quantum number  $-3$  is

  - a. 4
  - b. 3
  - c. 2
  - d. 1

77. The correct order of number of unpaired electrons in the ion  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  is

  - a.  $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Cr}^{3+} > \text{Fe}^{3+}$
  - b.  $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+} > \text{Cr}^{3+}$
  - c.  $\text{Fe}^{3+} > \text{Cr}^{3+} > \text{Ni}^{2+} > \text{Cu}^{2+}$
  - d.  $\text{Fe}^{3+} > \text{Cr}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+}$

78. In which of the following case would the probability of finding an electron residing in a  $d_{xy}$  orbital be zero?

  - a.  $xz$  and  $yz$ -planes
  - b.  $xy$  and  $yz$ -planes
  - c.  $z$ -direction,  $yz$  and  $xz$ -planes
  - d.  $xy$  and  $xz$ -planes

- 79.** A monoenergetic electron beam with a de Broglie wavelength of 'P' Å is accelerated till its wavelength is halved. By what factor will its kinetic energy change?

  - a. 2
  - b.  $\frac{1}{2}$
  - c. 4
  - d. Remains same

**80.** The first emission line in the atomic spectrum of hydrogen in the Balmer series appears at:

  - a.  $\frac{3R}{4}$  cm $^{-1}$
  - b.  $\frac{5R}{36}$  cm $^{-1}$
  - c.  $\frac{36}{5R}$  cm $^{-1}$
  - d.  $\frac{7R}{36}$  cm $^{-1}$

**81.** The isoelectronic pair is:

  - a.  $\text{ClO}_2^-$ ,  $\text{ClF}_2^+$
  - b.  $\text{IF}_2^+$ ,  $\text{I}_3^-$
  - c.  $\text{Cl}_2\text{O}_3$ ,  $\text{ICl}_2^-$
  - d.  $\text{ICl}_2^-$ ,  $\text{ClO}_2$

**82.** If Aufbau rule is not followed then percent change in total  $(n + l)$  value for unpaired electrons in  ${}_{25}\text{Mn}$  is:

  - a. 60
  - b. 50
  - c. 40
  - d. 30

**83.** A photon of wavelength 300 nm is absorbed by a gas and then re-emitted as two photons. One photon is red with wavelength of 760 nm. The wave number of the second photon will be

  - a.  $2.20 \times 10^7$  m $^{-1}$
  - b.  $2.02 \times 10^6$  m $^{-1}$
  - c.  $4.04 \times 10^7$  m $^{-1}$
  - d.  $1.01 \times 10^6$  m $^{-1}$

**84.** The de Broglie wavelength associated with a ball of mass 1 kg having a kinetic energy 0.5 J is

  - a.  $6.626 \times 10^{-34}$  m
  - b.  $13.2 \times 10^{-34}$  m
  - c.  $10.38 \times 10^{-21}$  m
  - d. 6.626 Å

**85.** If uncertainty in position and momentum are equal, then uncertainty in velocity is:

  - a.  $1/m \sqrt{(h/\pi)}$
  - b.  $\sqrt{(h/\pi)}$
  - c.  $1/2m \sqrt{(h/\pi)}$
  - d.  $\sqrt{(h/2\pi)}$

**86.** What is the wavelength of the radiation emitted producing in a line in the Lyman series when an electron falls from fourth stationary state in hydrogen atom? ( $R_H = 1.1 \times 10^7$  m $^{-1}$ )

  - a. 96.97 nm
  - b. 969.7 nm
  - c. 0.9697 nm
  - d. none

**87.** If the shortest wavelength of hydrogen atom in Lyman series is X, then longest wavelength in Paschen series of  $\text{He}^+$  is

a.  $\frac{36 \times}{5}$

c.  $\frac{7 \times}{36}$

b.  $\frac{36 \times}{7}$

d.  $\frac{6 \times}{5}$

88. In the consideration of the Bohr theory for the hydrogenic species, which electron orbit of the  $\text{Be}^{3+}$  ion can have the same radius as the ground state electron orbit of the hydrogen atom?

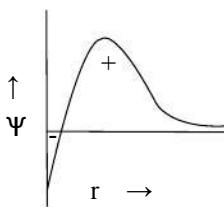
a. 1

c. 3

b. 2

d. 4

89. Wave function vs distance from nucleus graph of an orbital is given below



The number of nodal (sphere) of this orbital is

a. Zero

b. 1

c. 2

d. Can't be said

90. The electronic configuration of four elements P, Q, R and S given below. Choose the element that would most readily form a diatomic molecule.

$P = 1s^2 2s^2 2p^1$ ,  $Q = 1s^2 2s^2 2p^5$

$R = 1s^2 2s^2 2p^6 3s^1$ ,  $S = 1s^2 2s^2 2p^2$

a. Q

b. S

c. P

d. R

91. Consider the following sets of quantum numbers:

	n	l	m	s
(1)	3	0	0	$-\frac{1}{2}$
(2)	2	2	2	$-\frac{1}{2}$
(3)	4	3	-2	$-\frac{1}{2}$
(4)	1	0	-1	$-\frac{1}{2}$
(5)	3	2	3	$+\frac{1}{2}$

Which of the following sets of quantum number is not possible?

a. 2, 3 and 4

b. 1, 2, 3 and 4

c. 2, 4 and 5

d. 1 and 3

92. An atom A has the electronic configuration of  $1s^2 2s^2 2p^1$ . Atom B has the electronic configuration of  $1s^2 2s^2 2p^3$ . The empirical formula of the compound obtained from the reaction of A and B is

a. AB

c.  $A_3B_3$ b.  $AB_3$ d.  $A_2B_6$ 

93. The atomic numbers of elements X, Y, Z are 19, 21 and 25 respectively. The number of electrons present in the 'M' shells of these elements follow the order

a.  $Z > Y > X$ c.  $Z > X > Y$ b.  $X > Y > Z$ d.  $Y > Z > X$ 

94. Hydrogen atoms are excited on  $n = 4$  state. In the spectrum of emitted radiation, number of lines in the ultraviolet and visible regions are respectively

a. 3 : 2

c. 1 : 3

b. 3 : 1

d. 2 : 3

95. Photoelectric emission is observed from a surface for frequencies  $v_1$  and  $v_2$  of the incident radiation ( $v_1 > v_2$ ). If the maximum kinetic energies of the photoelectrons in the two cases are in the ratio  $1 : k$  then the threshold frequency  $v_0$  is given by

a.  $\frac{kv_2 - v_1}{k-1}$

b.  $\frac{v_2 - v_1}{k}$

c.  $\frac{v_2 - v_1}{k-1}$

d.  $\frac{kv_1 - v_2}{k-1}$

96. A light source of wavelength ( $\lambda$ ) illuminates a metal and ejects photoelectrons with  $(\text{K.E.})_{\text{max}} = 1 \text{ eV}$

Another light source of wavelength  $\lambda/3$ , ejects photoelectrons from same metal with  $(\text{K.E.})_{\text{max}} = 4 \text{ eV}$

Find the value of work function?

a. 1 eV

c. 1.5 eV

b. 0.5 eV

d. 2.5 eV

97. The ionization energy of  $\text{He}^+$  is  $19.6 \times 10^{-18} \text{ J atom}^{-1}$ . Calculate the energy of the first stationary state of  $\text{Li}^{2+}$ .

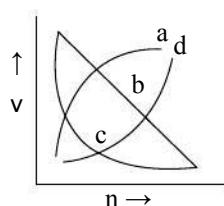
a.  $19.6 \times 10^{-18} \text{ J atom}^{-1}$

b.  $4.41 \times 10^{-18} \text{ J atom}^{-1}$

c.  $19.6 \times 10^{-19} \text{ J atom}^{-1}$

d.  $4.41 \times 10^{-17} \text{ J atom}^{-1}$

98. Which of the following curves may represent the speed of the electron in a hydrogen atom as a function of the principal quantum number n?



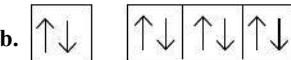
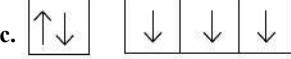
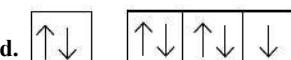
a. d

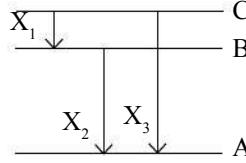
c. b

b. c

d. a

### 3.38 ■ Atomic Structure

99. Energy of H-atom in the ground state is -13.6 eV, hence energy in the second excited state is  
 a. -6.8 eV      b. -3.4 eV  
 c. -1.51 eV      d. -4.53 eV
100. Among the following series of transition metal ions, the one where all metal ion have  $3d^2$  electronic configuration is  
 a.  $Ti^{3+}$ ,  $V^{2+}$ ,  $Cr^{3+}$ ,  $Mn^{4+}$   
 b.  $Ti^{+}$ ,  $V^{4+}$ ,  $Cr^{6+}$ ,  $Mn^{7+}$   
 c.  $Ti^{4+}$ ,  $V^{3+}$ ,  $Cr^{2+}$ ,  $Mn^{3+}$   
 d.  $Ti^{2+}$ ,  $V^{3+}$ ,  $Cr^{4+}$ ,  $Mn^{5+}$   
 (At. wt. Ti = 22; V = 23; Cr = 24; Mn = 25 )
101. The orbital diagram in which both the pauli's exclusion principle and Hund's rule are violated is
- a. 
- b. 
- c. 
- d. 
102. In Bohr series of lines of hydrogen spectrum, the third line from the red end corresponds to which one of the following inter-orbit jumps of the electron for Bohr orbits in an atom of hydrogen?  
 a.  $3 \rightarrow 2$       b.  $5 \rightarrow 2$   
 c.  $4 \rightarrow 1$       d.  $2 \rightarrow 5$
103. The first orbital of H is represented by:  

$$\psi = \frac{1}{\sqrt{\pi}} (1/a_0)^{3/2} e^{-r/a_0}$$
- Here,  $a_0$  is Bohr's radius. The probability of finding the electron at a distance  $r$ , from the nucleus in the region  $dV$  is:  
 a.  $\psi^2 4\pi r^2 dr$       b.  $\int \psi dV$   
 c.  $\psi^2 dr$       d.  $\int \psi^2 4\pi r^2 dV$
104. Which orbital has only positive value of wave function at all distances from the nucleus?  
 a. 3d      b. 2p  
 c. 2s      d. 1s
105. Which of the following sets of quantum numbers is correct for an electron in 4f orbital?  
 a.  $n = 4, l = 3, m = +4, s = +\frac{1}{2}$   
 b.  $n = 4, l = 4, m = -4, s = -\frac{1}{2}$   
 c.  $n = 4, l = 3, m = +1, s = +\frac{1}{2}$   
 d.  $n = 3, l = 2, m = -2, s = +\frac{1}{2}$
106. Consider the ground state of Cr atom ( $Z = 24$ ). The numbers of electrons with the azimuthal quantum numbers,  $l=1$  and 2 are, respectively:  
 a. 12 and 4      b. 12 and 5  
 c. 16 and 4      d. 16 and 5
107. In the Bohr's orbit, what is the ratio of total kinetic energy and the total energy of the electron?  
 a. +1      b. +2  
 c. -2      d. -1
108. The angular momenta of 2s and 2p electrons, in units of  $h/2\pi$ , are respectively  
 a. 1, 2      b. 2, 2  
 c.  $0, \sqrt{2}$       d. 0, 1
109. The wavelength of the radiation emitted, when in a hydrogen atom electron falls from infinity to stationary state 1, would be (Rydberg constant =  $1.097 \times 10^7 \text{ m}^{-1}$ ):  
 a. 91 nm      b. 192 nm  
 c. 406 nm      d.  $9.1 \times 10^{-8} \text{ nm}$
110. Energy levels A, B, C of a certain atom corresponds to increasing values of energy, i.e.,  $E_A < E_B < E_C$ . If  $X_1$ ,  $X_2$  and  $X_3$  are the wavelengths of radiations corresponding to the transitions C to B, B to A and C to A respectively, which of the following statement is correct?
- 
- a.  $X_1 + X_2 + X_3 = 0$   
 b.  $X_3 = X_1 + X_2$   
 c.  $X_3^2 = X_1^2 + X_2^2$   
 d.  $X_3 = \frac{X_1 X_2}{X_1 + X_2}$ .
111. The Balmer-Rydberg equation can be extended to ions with only one electron, such as  $He^+$ . In that case it has the form:

$1/\lambda = Z^2 R (1/m^2 - 1/n^2)$ , here Z is the atomic number. What is the energy of the photon required to promote an electron in  $\text{He}^+$  from a 1s-orbital to a 2p-orbital?

- a.  $12 \text{ hcR}$
- b.  $6 \text{ hcR}$
- c.  $3 \text{ hcR}$
- d.  $(3/4) \text{ hcR}$

112. A beam of protons is accelerated through a potential drop of 200 volts. The same experiment is done with a beam of deuterons. After acceleration each beam is bent by the same magnetic field in a directions perpendicular to that of the beam. Which beam will exhibit the greater curvature?

- a. The same curvature for both
- b. The beam with the larger velocity will exhibits the smaller curvature
- c. The proton beam
- d. The deuteron beam

113. The numerical value  $\psi_{4,2,0}$  denotes

- a.  $4dx^2y^2$
- b.  $4dz^2$
- c.  $4p_z$
- d.  $4f_{xyz}$

114. In the Bohr's model of the hydrogen atom, which of the following statements is correct?

- a. The transition  $n = 1 \rightarrow n = 3$  represents absorption of energy
- b. The transition  $n = 2 \rightarrow n = 4$  represents emission of energy
- c. When  $n = \infty$ , the electron is in its ground state
- d. When  $n = 1$ , the electron is in an excited state

115. The number of photons of light having wave number 'a' in 3 J of energy source is

- a.  $hc/3a$
- b.  $3hca$
- c.  $3a/hc$
- d.  $3/hca$

116. The wavelength of the de Broglie wave of the electron revolving in the sixth orbit of the hydrogen atom is

- a.  $\pi r_0$
  - b.  $12\pi r_0$
  - c.  $6\pi r_0$
  - d.  $24\pi r_0$
- ( $r_0$  is the Bohr's radius = 0.529 Å)

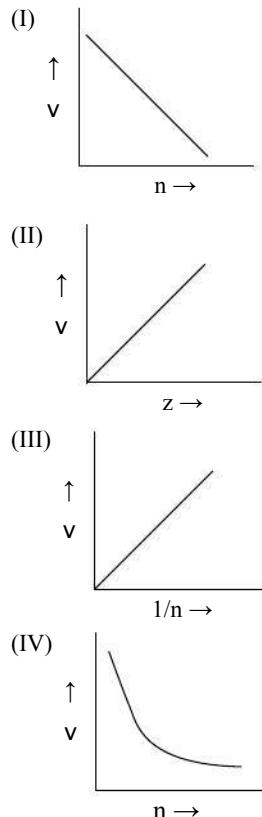
117. For an electron in a hydrogen atom, the wave function,  $\psi$  is proportional to  $\exp(-r/a_0)$ , where  $a_0$  is the Bohr's radius. What is the ratio of probability of finding electron at the nucleus to the probability of finding it at 90°?

- a. Zero
- b. e
- c.  $e^2$
- d.  $1/e^2$

118. The masses of photons corresponding to the first lines of the Lyman and the Balmer series of the atomic spectrum of hydrogen are in the ratio of

- a. 4 : 9
- b. 27 : 5
- c. 9 : 4
- d. 1 : 1

119. Select the correct graph for velocity of  $e^-$  in an orbit vs Z,  $1/n$  and n:



- a. I and II
- b. II and IV
- c. I, II and IV
- d. II, III and IV

120. A mono electronic species in energy level with energy 'X' was provided with excess of energy so that it jumps to higher energy level with energy 'Y'. If it can emit 6 wavelengths originated from all possible transition between these group levels, then which of the following relation is correct?

- a.  $X/Y = (n - 1)^2$
- b.  $X/Y = 1 + 3/n$
- c.  $\sqrt{(X/Y)} = 1 + 3/n$
- d.  $X/Y = n/6$

(Here n is the principal quantum number of energy level X)

### Multiple Correct Answer Type Questions

121. Bohr's model of atom cannot explain
- Zeeman effect
  - Stark effect
  - Linear spectrum of hydrogenic species
  - Fine spectrum of hydrogenic species
122. Select the correct statement(s) about Uncertainty principle.
- The product of uncertainty in momentum in position is always constant
  - This principle can explain why electron cannot exist in nucleus
  - This principle is applicable to microscopic as well as macroscopic particle
  - Heisenberg uncertainty principle is ruled out the concept of definite trajectories around the nucleus.
123. Which of the following is/are true in Rutherford's nuclear model of atom?
- The number of protons and neutrons are always equal
  - The number of electrons and protons are always equal
  - Protons and neutrons are present inside the nucleus
  - Volume of nucleus is very small as compared to the volume of atom
124. Which of the following statement is/are correct?
- In silver atom, 23 electrons have a spin of one type and 24 of the opposite (atomic number of Ag = 47)
  - The number of unpaired electrons in both  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  are five
  - The electronic configuration of Cr is  $[\text{Ar}] 3\text{d}^4 4\text{s}^1$  (atomic number of Cr = 24)
  - The azimuthal quantum number may have a negative value.
125. Which of the following statement(s) is/are correct?  
An atomic orbital
- Describes trajectory of electron in an atom
  - Is a single electron wave function
  - Can be represented by boundary surface diagrams
  - Defines distribution of electron density in space
126. The kinetic energy of photoelectron emitted on irradiating a metal surface with frequency  $v$  is related

by  $\text{KE} = hv - \text{IE}$ . The plots of KE vs. incidented frequency  $v$  shows:

- A straight line with slope equal to Planck's constant.
  - A straight line with intercept on x-axis equal to the product of threshold frequency and Planck's constant.
  - A straight line with extrapolated intercept on y-axis equal to ionization energy
  - A straight line with intercept on x-axis equal to threshold frequency
127. Which of the following statements is/are correct?
- Energy of the electron in hydrogen like atom/ion at infinite distance is zero and yet it is maximum
  - The position and momentum of a rolling ball can be measured accurately
  - Some spectral lines of an element may have the same wave number
  - Probabilities are found by solving Schrodinger wave equation
128. Which of these represent possible arrangement(s)?
- | n    | l | m  | s              |
|------|---|----|----------------|
| a. 2 | 1 | -1 | $\frac{1}{2}$  |
| b. 3 | 0 | 0  | $-\frac{1}{2}$ |
| c. 3 | 2 | -3 | $\frac{1}{2}$  |
| d. 5 | 3 | -2 | $-\frac{1}{2}$ |
129. Which of the following statement(s) is/are correct for orbital angular momentum of 2p and 3p-electron?
- Orbital angular momentum of 3p-electron is more than that of 2p-electron
  - Orbital angular momentum of 2p-electron is more than that of 3p-electron
  - Orbital angular momentum of 2p electron is equal to 2s electron and 3p electron is equal to 3s electron
  - Orbital angular momentum of 2p-electron is same as that of 3p-electron
130. Which set of quantum number is consistant with theory?
- $n = 2, l = 1, m = 0, s = -\frac{1}{2}$
  - $n = 4, l = 3, m = 2, s = -\frac{1}{2}$
  - $n = 3, l = 2, m = 3, s = +\frac{1}{2}$
  - $n = 4, l = 3, m = 3, s = +\frac{1}{2}$

131. Which among the following are impossible arrangements of quantum numbers?

	n	l	m	s
a.	3	1	-2	+ ½
b.	3	3	-1	- ½
c.	4	0	0	+ ½
d.	3	2	-3	- ½

132. Which of the following statements may be regarded as indicating a defect of the Bohr theory of the hydrogen spectrum?

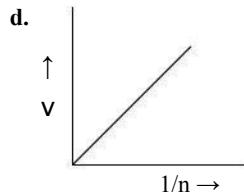
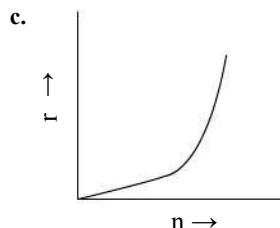
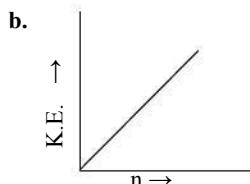
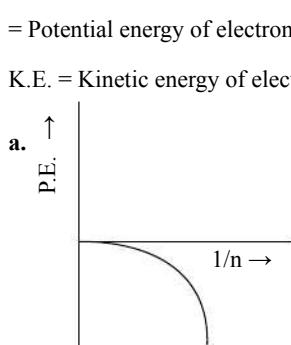
- a. The theory could not be extended to polyatomic atoms.
- b. The theory bypassed classical electromagnetism which states that orbiting electrons should spiral around the nucleus and fall in.
- c. The theory had nothing to say about the intensities of spectral lines.
- d. The theory ignored the wave nature of the electrons.

133. The ratio of the de-Broglie wavelengths of an  $\alpha$ -particle and a proton can be 2 : 1 when

- a. Their velocities are in 4 : 1 ratio
- b. Their velocities are in 8 : 1 ratio
- c. Their kinetic energies are in 128 : 1 ratio
- d. Their kinetic energies are in 256 : 1 ratio.

134. Select the correct curve(s):

If  $v$  = Velocity of electron in Bohr's orbit  
 $r$  = Radius of electron in Bohr's orbit  
 $P.E.$  = Potential energy of electron in Bohr's orbit



135. Which of the following is/are correct?

- a. the energy of an electron depends only on the principal quantum number not on the other quantum numbers
- b. the energy of an electron depends only on the principal quantum number in case of hydrogen and hydrogen like atoms.
- c. the difference in potential energies of any two energy level is always more than the difference in kinetic energies of these two levels.
- d. an electron in an excited state can always emit a photon or two but can not absorb a photon

136. The angular momentum of any electron can have the value(s)

- |                 |                  |
|-----------------|------------------|
| a. $3(h/\pi)$   | b. $2.5(h/2\pi)$ |
| c. $0.5(h/\pi)$ | d. $(h/\pi)$     |

137. Which of the following statements in relation to the hydrogen atom is incorrect?

- a. 3s and 3p orbitals are of lower energy than 3d orbital
- b. 3p orbital is lower in energy than 3d orbital
- c. 3s orbital is lower in energy than 3p orbital
- d. 3s, 3p and 3d orbitals all have the same energy

138. Which of the following statements are false?

- a. the uncertainty in position and momentum in Heisenberg's principle due to electron wave
- b. the energy level order  $4s < 3d < 4p < 5s$  may not hold good for all elements
- c. the quantum number of light radiation is manifested in photoemission of electrons
- d. according to Bohr's theory the energy decreases as  $n$  increases.

139. Five valence electrons of  $_{15}P$  are labelled as

Pq	x	y	z
3s	3p		

### 3.42 ■ Atomic Structure

If the spin quantum number of q and z is +  $\frac{1}{2}$   
The group of electrons with three of the quantum number same are

- a. Pq
- b. (xyz), (Pq)
- c. (Pq), (xyz), (Pz)
- d. (Pq), (xyz), (qy)

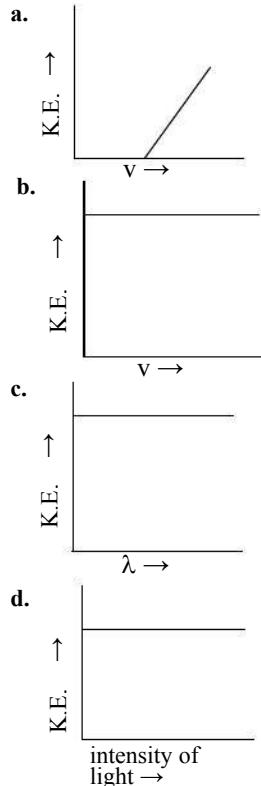
140. Which of the following statement(s) about spectral series is/are correct?

- a. Paschen series appears in the infrared region
- b. The lines in the Balmer series corresponds to electron transitions from energy levels higher than n = 2 energy level.
- c. Transitions from higher energy levels to 5<sup>th</sup> energy level produce Pfund series which falls in the infrared region
- d. The lines of Lyman series appear in the visible region

141. Which of the following are the limitations of Bohr's model?

- a. It can not be applied to hydrogenic species
- b. It can not explain the intensities or the fine spectrum
- c. It can not explain the principle of quantization of angular momentum.
- d. It can not explain circular orbit concept

142. Which do not represent correct graph(s) here?



143. Which of the following statement is/are correct regarding angular nodes?

- a. They are independent from the radial wave function (R)
- b. They are directional in nature
- c. They are dependent on the radial wave function
- d. They are dependent on angle  $\theta$  and  $\phi$ .

144. The correct matching is shown by

- a. Wave mechanical model: The electron finding probability for 2s orbital in H-atom is zero at  $r = a_0$  where  $a_0 = 0.53 \text{ \AA}$ .
- b. Bohr's model: The angular momentum of electron in first excited state of H-atom is  $5\hbar/11$
- c. Rutherford's model : Very few  $\alpha$ -particles get deflected by large angles because nucleus has much smaller volume than that of atom
- d. Thomson's model: The electrons on disturbing by collision vibrate around their mean position and emit electromagnetic radiation.

145. Which of the following statement(s) is/are correct?

- a. Planck's study of black-body radiation led to the hypothesis that radiation is emitted in quanta of energy
- b. Photons of lower frequency radiation have lower energies.
- c. Bohr's model of the hydrogen atom showed emission of energy by atoms occurs when an electron moves to a higher orbit.
- d. The lowest energy state of an electron in an atom is known as the ground state

146. Which of the following match is/are correct?

- |                 |                       |
|-----------------|-----------------------|
| a. 4f orbital   | (maximum 2 electrons) |
| b. 4s orbital   | (2 radial nodes)      |
| c. 3dxy orbital | (2 nodal planes)      |
| d. 5px orbital  | (2 radial nodes)      |

147. Which of the following is/are not correctly matched?

- a. e/m ratio of anode rays : Independent of gas in the discharge tube
- b. Radius of nucleus :  $(\text{Mass number})^{1/2}$
- c. Momentum of H-atom when electrons returns from n = 2 to n = 1 :  $3Rh/4$
- d. Momentum of photon : Independent of wave length of light

148. Select the correct statement(s):

- a. Gravitation has a rest mass zero but spin 2 and it is exchanged during gravitational interaction between bodies

- b.** Rest mass of photon is zero and increases with its velocity

**c.** Photons are carrier of energy, momentum and angular momentum between interacting particles

**d.** Mass of a p-meson is about 276 times of an electron and it keeps nucleons together

**149.** Which statement is/are true for many electron atoms?

  - The  $2P_x$  and  $2P_y$  orbitals have the same energy in the absence of an applied magnetic field
  - The  $2s$  and  $2p$  orbitals are of differing energies, whereas in a hydrogen atom they are same.
  - Outer electrons penetrate the electron clouds of inner electrons
  - Outer electrons experience the full nuclear charge

**150.** Regarding the atomic orbital  $\psi_{1s}$  of the hydrogen atom, which of the following statements is/are true?

  - $\psi_{1s}$  has no nodal plane.
  - $\psi_{1s}$  has a non-zero value at the nucleus
  - $[\psi_{1s}]^2$  is a measure of the probability per unit volume of locating the electron.
  - The magnitude of  $\psi_{1s}$  is experimentally measurable.

**c.** Position on electron

**d.** Charge on electron.

**154.** In an orbit the velocity of an electron in excited state of H-atom is  $1.093 \times 10^8$  cm / s . What is the circumference in this orbit.

  - 6.65 Å
  - 13.3 Å
  - 3.33 Å
  - 26.65 Å

## Comprehension 2

An electromagnetic radiation is emitted when an electric discharge is passed through  $H_2$  gas. When passed through a prism of diffraction grating, this radiation is found to have a series of components in U.V, visible, and Infrared regions. Rydberg used the relation  $\frac{1}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$  to find wavelength.

Here  $R_H$  = Rydberg's constant ( $1.1 \times 10^7$  m<sup>-1</sup>)

**155.** Same wavelength is observed with respect to Li<sup>2+</sup> from a transition of  $n_2 = 6$  to  $n_1 = 3$

  - $4 \rightarrow 2$  of Be<sup>3+</sup>
  - $3 \rightarrow 1$  of H-atom
  - $4 \rightarrow 2$  of He<sup>+</sup>
  - $4 \rightarrow 2$  of He-atom

**156.** The wave motion of an electron in a Bohrs Orbic of

## **Linked-Comprehension Type Questions**

## Comprehension 1

Elements are composed of tiny particles known as atoms. Atoms are made of fundamental particles ( $e$ ,  $p$ ,  $n$ ). According to Rutherford's Atomic Model  $p$ ,  $n$  are located in Nucleus. Bohr's model explained the existence of circular orbits (energy levels) around the nucleus. Bohr's model can explain the spectrum of hydrogenic species and helps in find  $e$ ,  $v$ ,  $r$  (energy, velocity and radius) in  $n$ th orbit.

- 151.** The ratio of  $r_4$  and  $r_3$  for hydrogen atom and that of  $\text{Li}^{+2}$  ion

a. 1 : 3                          b. 3 : 1  
c. 1 : 9                          d. 1 : 1

**152.** The value of electro static potential energy =

a.  $mv^2$                           b.  $\frac{ze^2}{r}$   
c.  $\frac{1}{4\pi\epsilon_0} \times \frac{q_1 q_2}{r}$                   d.  $\frac{1}{4\pi\epsilon_0} \frac{ze^2}{r}$

**153.** Suppose Rutherford had used electron in place of alpha - particles. Then what conclusion is achieved

a. Wave nature of electron  
b. Specific charge on electron



## Comprehension 2

An electromagnetic radiation is emitted when an electric discharge is passed through H<sub>2</sub> gas. When passed through a prism or diffraction grating, this radiation is found to have a series of components in U.V., visible, and Infrared regions. Rydberg used the relation  $\frac{1}{\lambda} =$

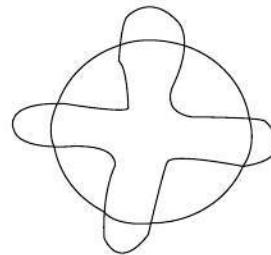
$R_H \left( \frac{1 - 1}{n_1^2 - n_2^2} \right)$  to find wavelength.

Here  $R_H$  = Rydberg's constant ( $1.1 \times 10^7 \text{ m}^{-1}$ )

- 155.** Same wavelength is observed with respect to Li<sup>2+</sup> from a transition of n<sub>2</sub> = 6 to n<sub>1</sub> = 3

a. 4 → 2 of Be<sup>+3</sup>      b. 3 → 1 of H-atom  
c. 4 → 2 of He<sup>+</sup>      d. 4 → 2 of He-atom

**156.** The wave motion of an electron in a Bohrs Orbic of Hydrogen atom can be shown by the figure given below find potential energy



- 157.** The Balmer-Rydberg equation can be extended to ions with only one electron, such as  $\text{He}^+$ . In that case it has the form:

$$1/\lambda = Z^2 R (1/m^2 - 1/n^2)$$
, here  $Z$  is the atomic number. What is the energy of the photon required to promote an electron in  $\text{He}^+$  from a 1s-orbital to a 2p-orbital?

## 3.44 ■ Atomic Structure

- a. 2.86 .4 nm
- b. 584.6 nm
- c. 486.2 nm
- d. 648.2 nm

### Comprehension 3

The ground state electronic Configuration of a multielectron atom is possible by using these rules.

- i. The lowest energy orbital is filled first (Aufbau).
  - ii. Any orbital can have max.  $2e^-$  having opposite spin (Pauli).
  - iii. In case of degenerate orbitals each is half filled before any of these is completely filled (Hund's Rule).
159. Which of the following represent electron configuration that violate the Pauli exclusion principle?

- I. [Ne]  $3s^1 3p^5$
  - II. [Kr]  $4d^{12} 5s^2 5p^3$
  - III. [Ar]  $3d^{10} 4s^2 4p^2$
- a. Only (II)
  - b. Only (I)
  - c. Both (I) and (III)
  - d. Both (II) and (III)

160. List all the elements that have a ground state configuration with five unpaired electrons in the 3d-subshell.

- a. Mn
- b. Cr
- c. Cr and Mn
- d. Mn, Fe, Co,

161. Which have the largest number of unpaired electrons in p-orbitals in their ground state electronic configurations?

- a. Te, I, Xe
- b. F, Cl, Br
- c. Ne, Ar, Kr
- d. N, P, As

162. Which of the following represent electronic configurations that are allowed but do not represent ground-state configurations?

- I. [Ne]  $3s^1 3p^5$
  - II. [Kr]  $4d^{12} 5s^2 5p^3$
  - III. [Ar]  $3d^{10} 4s^2 4p^2$
- a. I and II
  - b. II and III
  - c. only II
  - d. only I

### Comprehension 4

Schrodinger proposed Quantum Mechanical model in 1926. He described an atom by an equation similar to that used to explain wave motion. The behaviour of each electron in an atom is characterized by a wave function

( $\Psi$ ).  $\Psi^2$  defines the probability of finding the electron in a given volume of space. Each wave function has a set of three variable known as Quantum Numbers (n, l, m).

163. Select the correct statements.

- i. At a node the wavefunction  $\Psi$  has zero amplitude.
  - ii. the number of peaks (maxima) in radial distribution.
  - iii.  $\Psi$  is (n-l) represents probability of finding electrons and it is direction independent.
  - iv.  $\Psi$  4, 2, 0 stands for  $4d_{z^2}$
- a. i, ii, iii
  - b. i, ii , iv
  - c. ii, iii, iv
  - d. i, ii, iii, iv

164. For a particular orbital, as one goes away from the nucleus along the Z-axis, the probability density decreases to zero, then increases, and finally decreases without increasing a second time. This is consistent with a

- a.  $2p_z$  orbital
- b. 2s orbital
- c. 3s-orbital
- d. 2s or 2Pz orbital

165. Which orbitals have two nodal planes passing through the nucleus?

- a. d
- b. p
- c. s
- d. All in the third shell

### Assertion-Reason Type Questions

In the following questions, two statements (Assertion) A and Reason (R) are given. Mark

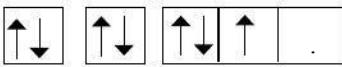
- a. If A and R both are correct and R is the correct explanation of A
- b. If A and R both are correct but R is not the correct explanation of A
- c. A is true but R is false
- d. A is false but R is true
- e. A and R both are false

166. (A): The shortest wavelength of transition of Lyman series is observed when electron jumps from orbit number,  $n = \infty$  to  $n = 1$ .

(R): Since the wavelength of transition is given by  $hc/\lambda = \Delta E$

167. (A): The kinetic energy of the photo-electron ejected increases with increase in intensity of incident light.

(R): Increase in intensity of incident light increases the rate of emission.

- 168.** (A): Limiting line in the Balmer series of H-spectrum has a wavelength of 364.4 nm.  
 (R): Limiting line is obtained for a jump of electron from  $n = \infty$  to  $n = 2$ .
- 169.** (A):  $3dZ^2$  orbital is spherically symmetrical.  
 (R):  $3dZ^2$  orbital is the only d-orbital which is spherical in shape.
- 170.** (A): Shapes of the orbitals are represented by boundary surface diagrams of contrast probability density.  
 (R): Boundary surface diagram helps in interpreting and visualizing an atomic orbital.
- 171.** (A): Half-filled and fully-filled degenerate orbitals are more stable.  
 (R): Extra stability is due to the symmetry of degenerate orbitals.
- 172.** (A): A spectral line will be observed for a  $2p_x - 2p_y$  transition.  
 (R): The energy is released in the form of wave of light when electron drops from  $2p_x$  to  $2p_y$  orbital.
- 173.** (A): The angular momentum of d-orbital is  $\sqrt{6} h/2\pi$   
 (R): d-orbitals have double dumb-bell shaped except  $d_{z^2}$ .
- 174.** (A): Electron can have wavelength equal to that of proton of  $V_e = 1836 V_p$ .  
 (R): Electron has mass  $1/1836$  of the mass of proton.
- 175.** (A): The kinetic energy of photoelectrons increases with increase in frequency of incident light.  
 (R): The number of photoelectron ejected increases with increase in intensity of light.
- 176.** (A): Fluorescence is the emission of light which has been absorbed by the molecule  
 (R): It may continue for appreciable time after the exciting light is switched off.
- 177.** (A):  $Fe^{2+}$  has 24 electrons hence, its electronic configuration, is similar to that of Cr(24) [Ar]  $3d^5 4s^1$ .  
 (R): All the five unpaired electrons in 3d gives stability to the ion.
- 178.** (A): On heating a solid for a longer time, radiations become white and then blue as the temperature becomes very high.  
 (R): Radiations emitted go from a lower frequency to higher frequency as the temperature increases.
- 179.** (A):  $Cu^{2+}$  is a coloured ion.  
 (R): Every ion with unpaired electron is coloured.
- 180.** (A): The paramagnetism of  $Cu^+$  ion is zero.  
 (R): Paramagnetism is given by the relation  $\mu = \sqrt{S(S+1)}$  magnetons where S is the total spin.
- 181.** (A): Electrons are negatively charged.  
 (R): The application of electric and magnetic field deflected the rays in the discharge tube towards the cathode.
- 182.** (A): Electronic configuration of K (19) is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ .  
 (R): Energy of  $4s < 3d$  hence,  $4s$  is filled before  $3d$  as decided by Aufbau rule.
- 183.** (A): Atoms can neither be created nor destroyed.  
 (R): Under similar conditions of temperature and pressure, equal volumes of gases do not contain equal number of atoms.
- 184.** (A): For  $n = 3$ , l may be 0, 1 and 2 and m\_l may be 0;  $0 \pm 1$ ; 0,  $\pm 1$  and  $\pm 2$   
 (R): For each value of n, there are 0 to  $(n-1)$  possible values of l; and for each value of l, there are 0 to  $\pm 1$  values of m\_l.
- 185.** (A): The electronic configuration of nitrogen atom is represented as:  
 $1s^2 \quad 2s^2 \quad 2p^3$   
  
 and not as  
 $1s \quad 2s \quad 2p$   

- (R): The electronic configuration of the group state of an atom is the one which has the greatest multiplicity.

### Matrix-Match Type Questions

	p	q	r	s
A.	O	O	O	O
B.	O	O	O	O
C.	O	O	O	O
D.	O	O	O	O

### 3.46 ■ Atomic Structure

186. Match list I with list II and select the correct answer using the codes given below the lists.

<b>Column I (Metal ions)</b>	<b>Column II (Magnetic moment)</b>
A. Cr <sup>3+</sup>	(p) $\sqrt{35}$
B. Fe <sup>3+</sup>	(q) $\sqrt{8}$
C. Ni <sup>2+</sup>	(r) $\sqrt{24}$
D. Mn <sup>2+</sup>	(s) $\sqrt{15}$

187. Match the following:

<b>Column I (Principle)</b>	<b>Column II (Discoverer)</b>
A. Exclusion principle	(p) Hund
B. Multiplicity rule	(q) Heisenberg
C. Uncertainty principle	(r) Einstein
D. Quantum theory	(s) Planck
	(t) Pauli

188. Match the following:

<b>Column I</b>	<b>Column II</b>
A. Number of values of 'l' for an energy level ..... (n - 1)	(p) 0, 1, 2
B. Actual values of 'l' for a particular type of orbital	(q) +1 ..... +2, +1, 0, -1
C. Number of 'm' values	(r) -2, .... -1
D. Actual values of 'n' for a particular type of orbital	(s) n

189. Match the following:

<b>Column I</b>	<b>Column II</b>
A. Energy per molecule	(p) $E = h\nu$
B. Wave number	(q) $C/\lambda$
C. Frequency	(r) $1/\lambda$
D. Energy of one quantum	(s) $N h\nu$

190. Match the following:

<b>Column I</b>	<b>Column II</b>
A. Energy of e <sup>-</sup> in nth orbit	(p) $\propto n^2$
B. Wavelength of e <sup>-</sup> in nth orbit	(q) $\propto \frac{1}{n^2}$
C. Velocity of e <sup>-</sup> in nth orbit	(r) $\propto n$
D. Radius of e <sup>-</sup> in nth orbit	(s) $\propto \frac{1}{n}$

191. Match the following:

<b>Column I</b>	<b>Column II</b>
A. Principal quantum number	(p) Shape of orbital
B. Magnetic quantum number	(q) Orientation of orbital
C. Azimuthal quantum number	(r) Spinning of electron
D. Spin quantum number	(s) Size of orbital

192. Match the following:

<b>Column I</b>	<b>Column II</b>
A. 2s	(p) Sum of (n+1) is 3
B. 2p	(q) total number nodes are two
C. 3s	(r) only one node
D. 3p	(s) no radial node

193. Match the following:

<b>Column I</b>	<b>Column II</b>
A. Na	(p) Last valence e <sup>-</sup> in 3 <sup>rd</sup> orbit
B. Cl	(q) Last valence e <sup>-</sup> in 2 <sup>nd</sup> orbit
C. Li	(r) m-value is zero for last e <sup>-</sup>
D. Mg	(s) one un-paired e

194. Match the following:

<b>Column I</b>	<b>Column II</b>
A. He <sup>+</sup>	(p) 1s1 configuration
B. Li <sup>+2</sup>	(q) $\mu$ is 1.732 B.M
C. H-atom	(r) 0.529 Å value of radius in 1 <sup>st</sup> or 2 <sup>nd</sup> orbit
D. Be <sup>+3</sup>	(s) -13.6 e.v/atom energy in 1 <sup>st</sup> orbit

195. Match the following:

Column I	Column II
A. Cr	(p) $4s^1$ state Configuration state.
B. Cu	(q) Unpaired $e^-$ in $4s$ - orbit .
C. K	(r) Un-paired electron in $3d$ -orbital
D. Fe	(s) Ferro magnetic

### The IIT-JEE Corner

196. Among  $KO_2$ ,  $AlO_2^-$ ,  $BaO_2$  and  $NO_2^+$ , unpaired electron is present in

- a.  $NO_2^+$  and  $BaO_2$
- b.  $KO_2$  and  $AlO_2^-$
- c.  $KO_2$  only
- d.  $BaO_2$  only

[IIT 1997]

197. The first use of quantum theory of explain the structure of atom was made by

- |               |             |
|---------------|-------------|
| a. Heisenberg | b. Bohr     |
| c. Planck     | d. Einstein |

[IIT 1997]

198. Which of the following statement(s) are correct?

- 1. the electronic configuration of Cr is [Ar]  $3d^5 4s^1$  (atomic number of Cr = 24)
  - 2. the magnetic quantum number may have a negative value
  - 3. in silver atom, 23 electrons have a spin of one type and 24 of the opposite type (atomic number of Ag = 47)
  - 4. the oxiation state of nitrogen in  $HN_3$  is -3.
- |            |            |
|------------|------------|
| a. 1, 2, 3 | b. 2, 3, 4 |
| c. 3, 4    | d. 1, 2, 4 |

[IIT 1998]

199. One mole of calcium phosphide on reaction with excess of water gives

- a. one mole of phosphine
- b. two moles of phosphoric acid
- c. two moles of phosphine
- d. one mole of phosphorus pentoxide

[IIT 1999]

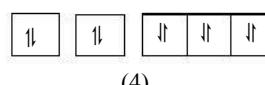
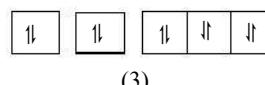
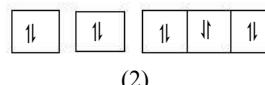
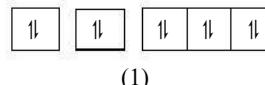
200. The electrons, identified by quantum numbers n and l (i)  $n = 4, l = 1$  (ii)  $n = 4, l = 0$  (iii)  $n = 3, l = 2$

(iv)  $n = 3, l = 1$  can be placed in order of increasing energy from the lowest to highest as

- a. (iv) < (ii) < (iii) < (i)
- b. (ii) < (iv) < (i) < (iii)
- c. (i) < (iii) < (ii) < (iv)
- d. (iii) < (i) < (iv) < (ii)

[IIT 1999]

201. Ground state electronic configuration of nitrogen atom can be represented by



- |           |         |
|-----------|---------|
| a. 1 only | b. 1, 2 |
| c. 1, 4   | d. 2, 3 |

[IIT 1999]

202. The quantum number  $+ \frac{1}{2}$  and  $- \frac{1}{2}$  for the electron spin represent

- a. rotation of the electron in clockwise and anti-clockwise direction respectively.
- b. rotation of the electron in anti-clockwise and clockwise direction respectively.
- c. magnetic moment of the electron pointing up and down respectively.
- d. two quantum mechanical spin states which have no classical analogues.

[IIT 2000]

203. The electronic configuration of an element is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ . This represents

- |                  |                 |
|------------------|-----------------|
| a. excited state | b. ground state |
| c. cationic form | d. anionic form |

[IIT 2000]

204. The number of nodal planes is a  $px$  orbital is

- |      |      |
|------|------|
| a. 1 | b. 2 |
| c. 3 | d. 0 |

[IIT 2000]

## 3.48 ■ Atomic Structure

- 205.** The wavelength associated with a golf ball weighing 200 g and moving at a speed of 5 m/h is of the order
- $10^{-10}$  m
  - $10^{-20}$  m
  - $10^{-30}$  m
  - $10^{-40}$  m
- [IIT 2001]
- 206.** How many moles of electrons weigh one kilogram?  
(mass of electron =  $9.108 \times 10^{-31}$  kg, Avogadro number =  $6.023 \times 10^{23}$ )
- $6.023 \times 10^{23}$
  - $1/9.108 \times 10^{31}$
  - $\frac{6.023}{9.108} \times 10^{54}$
  - $\frac{1}{9.108 \times 6.023} \times 10^8$
- [IIT 2002]
- 207.** If the nitrogen atom has electronic configuration  $1s^7$ , it would have energy lower than that of the normal ground state configuration  $1s^2 2s^2 2p^3$ , because the electrons would be closer to the nucleus. Yet  $1s^7$  is not observed because it violates.
- Heisenberg uncertainty principle
  - Hund's rule
  - Pauli's exclusion principle
  - Bohr postulates of stationary orbits.
- [IIT 2002]
- 208.** Rutherford's experiment, which established the nuclear model of the atom, used a beam of
- $\beta$ -particles, which impinged on a metal foil and got absorbed
  - $\gamma$ -rays, which impinged on a metal foil and ejected electrons
  - Helium atoms, which impinged on a metal foil and got scattered
  - Helium nuclei, which impinged on a metal foil and got scattered.
- [IIT 2002]
- 209.** An aqueous solution of 6.3 g of oxalic acid dihydrate is made upto 250 ml. The volume of 0.1 N NaOH required to completely neutralize 10 ml of this sol is
- 40 ml
  - 20 ml
  - 10 ml
  - 4 ml
- [IIT 2002]
- 210.** Which has maximum number of atoms?
- 24 g of C (12)
  - 56 g of Fe (56)
  - 27 g of Al (27)
  - 108 g of Ag (108)
- [IIT 2003]
- 211.** The radius of which of the following orbits is same as that of the first Bohr's orbit of hydrogen atom?
- $He^+$  ( $n = 2$ )
  - $Li^{2+}$  ( $n = 2$ )
  - $Li^{2+}$  ( $n = 3$ )
  - $Be^{3+}$  ( $n = 2$ )
- [IIT 2004]
- 212.** Radial nodes present in 3s and 2p-orbitals are respectively
- 0, 2
  - 2, 0
  - 2, 1
  - 1, 2
- [IIT 2005]
- 213.** Match the entries in **Column I** with the correctly related quantum number (s) in **Column II**.
- | <b>Column I</b>                                                                | <b>Column II</b>                 |
|--------------------------------------------------------------------------------|----------------------------------|
| (a) Orbital angular momentum of the electron in a hydrogen-like atomic orbital | (p) Principal quantum number     |
| (b) A hydrogen -like one-electron wave function obeying Pauli principle        | (q) Azimuthal quantum number     |
| (c) Shape, size and orientation of hydrogen-like atomic orbitals               | (r) Magnetic quantum number      |
| (d) Probability density of electron at the nucleus in hydrogen like atom       | (s) Electron spin quantum number |
- [IIT 2005]

## ANSWERS

### Straight Objective Type Questions

1. c	2. a	3. d	4. a	5. c	6. c	7. d	8. a	9. c
10. b	11. b	12. c	13. c	14. a	15. c	16. c	17. b	18. b
19. d	20. d	21. b	22. b	23. D	24. b	25. b	26. a	27. d
28. c	29. c	30. b	31. d	32. b	33. b	34. d	35. d	36. b
37. a	38. d	39. a	40. d	41. a	42. b	43. a	44. c	45. b
46. c	47. b	48. d	49. c	50. b	51. d	52. a	53. d	54. a
55. a	56. b	57. c	58. c	59. b	60. d	61. b	62. a	63. c
64. a	65. a	66. d	67. a	68. c	69. b	70. c	71. b	72. d
73. a	74. a	75. b						

### Brainteasers Objective Type Questions

76. a	77. c	78. a	79. c	80. b	81. a	82. c	83. b
84. a	85. c	86. a	87. b	88. b	89. b	90. a	91. c
92. a	93. a	94. a	95. d	96. b	97. d	98. b	99. c
100. d	101. a	102. b	103. a	104. d	105. c	106. b	107. d
108. c	109. a	110. d	111. c	112. c	113. b	114. a	115. d
116. b	117. a	118. b	119. d	120. c			

### Multiple Correct Answer Type Questions

121. a,b,d	122. a,b,d	123. b,c,d	124. a,c,d	125. b,c,d	126. a,c,d
127. a,b,d	128. a,b,d	129. a,b,c	130. a,b,d	131. a,d	132. a,c,d
133. b,d	134. a,c,d	135. b,d	136. a,c,d	137. a,b,c	138. b,d
139. a,b	140. a,b,c	141. b,c	142. b,c	143. a,b,d	144. b,c,d
145. a,b,d	146. a,b,c	147. a,b,d	148. a,b,c,d	149. a,b,c	150. a,b,c

### Linked-Comprehension Type Questions

#### Comprehension 1

151. b      152. c      153. a      154. b

#### Comprehension 4

163. b      164. b      165. a

#### Comprehension 2

155. c      156. b      157. c      158. c

#### Assertion Reason Type Questions

#### Comprehension 3

159. a      160. c      161. d      162. d

166. a	167. d	168. a	169. e
170. a	171. b	172. e	173. b
174. a	175. b	176. c	177. d
178. a	179. c	180. c	181. a
182. a	183. c	184. a	185. a

**Matrix-Match Type Questions**

- |                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                                                       |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>186.</b> A-(s), B-(r), C-(t), D-(p)<br><b>188.</b> A-(s), B-(p), C-(r), D-(q)<br><b>190.</b> A-(q), B-(r), C-(s), D-(p)<br><b>192.</b> A-(r, s), B-(p, r, s), C-(p, q, s), D-(q)<br><b>194.</b> A-(p, q), B-(p, q, r), C-(p, q), D-(p, q, r, s) | <b>187.</b> A-(t), B-(p), C-(q), D-(s)<br><b>189.</b> A-(s), B-(r), C-(q), D-(p)<br><b>191.</b> A-(s), B-(q), C-(p), D-(r)<br><b>193.</b> A-(p, r, s), B-(p, r, s), C-(q, r, s), D-(p, r)<br><b>195.</b> A-(p, q, r, s), B-(p, q), C-(p, q), D-(r, s) |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

**The IIT-JEE Corner**

- |               |                                      |               |               |               |               |               |               |
|---------------|--------------------------------------|---------------|---------------|---------------|---------------|---------------|---------------|
| <b>196.</b> c | <b>197.</b> b                        | <b>198.</b> a | <b>199.</b> c | <b>200.</b> a | <b>201.</b> c | <b>202.</b> d | <b>203.</b> b |
| <b>204.</b> a | <b>205.</b> c                        | <b>206.</b> d | <b>207.</b> c | <b>208.</b> d | <b>209.</b> a | <b>210.</b> a | <b>211.</b> d |
| <b>212.</b> b | <b>213.</b> A-q, B-s, C-p, q, r, D-p |               |               |               |               |               |               |

**Hints and Explanations****Straight Objective Type Questions**

3. Total values of  $m = (2l + 1)$  = no. of orbitals in subshell.  
As  $l = 2$  represents 'd' subshell and d subshell has five orbitals. ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ,  $d_x^2 - y^2$ ,  $d_z^2$ ).
8.  $M^{2+}$  has 5 unpaired electrons.  
Atomic number is 25.  
 $M \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$   
 $M^{2+} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5$
12. As  $Ni^{2+}$ ,  $Ti^{3+}$  has 2, 1 unpaired electrons respectively so both are coloured.
18.  $\Delta E = h\nu = h \frac{c}{\lambda}$ .  
 $\lambda = \frac{hc}{\Delta E}$   
i.e.,  $\lambda \propto 1/\Delta E$   
 $\Delta E = E_4 - E_1$  will be maximum and hence  $\lambda$  will be minimum.
21. I.E. of  $He^+ = 13.6 \text{ eV} \times Z^2$   
 $= 13.6 \text{ eV} \times 4 = 54.4 \text{ eV}$
32. The radius of nucleus is of the order of  $1.5 \times 10^{-13}$  to  $6.5 \times 10^{-13}$  cm or 1.5 to 6.5 Fermi (1 Fermi =  $10^{-13}$  cm)

33. It is  $Mn^{2+}$  having five unpaired electrons so its magnetic moment is  
 $\mu = \sqrt{5}(5+2)$   
 $= 5.9 \text{ BM.}$
34. Bohr model can explain spectrum of atoms/ions containing one electron only.
35. As circumference =  $n\lambda$   
 $= 4\lambda$
36. As  $N^{3-}$ ,  $F^-$  and  $Na^+$  have 10 electrons.
39. It is the 1s level, the ground state, where the H-atom can only absorb a photon and go to higher excited states.
41.  $^{28}\text{Ni} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$   
 $Ni^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$   
Hence d-electrons in Ni and  $Ni^{2+}$  are same.
42. Orbitals having same  $(n + l)$  value in the absence of electric and magnetic field will have same energy.
43. Rb has the configuration,  $1s^2 2s^2 2p^2 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$ ; so  $n = 5$ ,  $l = 0$ ,  $m = 0$  and  $s = \frac{1}{2}$
44.  $n = 3$ ,  $l = 0$  indicates last shell is 3s.

So electronic configuration will be  $1s^2\ 2s^2\ 2p^6\ 3s^{1-2}$

Atomic number is 11 or 12.

45. No. of lines =  $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$   
 $= \frac{(7-2)(7-2+1)}{2} = 15$

50. The central part consisting whole of the positive charge and most of the mass, called nucleus, is extremely small in size compared to the size of the atom.
53. The principal quantum number ( $n$ ) is related to the size of the orbital ( $n = 1, 2, 3, \dots$ )
56. As for s-orbital  $l = 0$
57. One p-orbital can accommodate up to two electrons with opposite spin while p-subshell can accommodate upto six electrons.
61. Rutherford's scattering experiment led to the discovery of nucleus.

62. Apply  
 $\Delta x \cdot \Delta v \geq \frac{\hbar}{4\pi m}$ .

64. Here  $Mn^{2+}$  has 5 unpaired electrons so it has maximum magnetic moment.

65.  $\lambda = h/mv$   
 $\lambda = \frac{6.626 \times 10^{-34}}{60 \times 10^{-3} \times 10} = 10^{-33} \text{ m (nearly)}$

67. As these have 18 electrons.

70. Number of electron in  $SO_3^{2-} =$

$$16 + 8 \times 3 + 2 = 42$$

$$\text{No. of } e^- \text{ in } CO_3^{2-} = 6 + 8 \times 3 + 2 = 32$$

$$\text{No. of } e^- \text{ in } NO_3^- = 7 + 8 \times 3 + 1 = 32$$

These are not isoelectronic species as number of electrons are not same.

72. As  $mvr = nh/2\pi$   
 $= 5h/2\pi = 2.5h/\pi$

### Brainteasers Objective Type Questions

77. As they have 5, 3, 2, 1 number of unpaired electrons respectively.

79.  $\lambda = \frac{h}{\sqrt{2mE}}$ .

$$\lambda E^{1/2} = \text{constant.}$$

$$\text{So } \lambda_1 \sqrt{E_1} = \lambda_2 \sqrt{E_2}$$

$$\lambda_1/\lambda_2 = \sqrt{(E_2/E_1)} = 2$$

$$\text{Therefore } E_2/E_1 = 4$$

80.  $\frac{1}{\lambda} = R \times 1^2 \left[ \frac{1}{2^2} - \frac{1}{3^2} \right]$

On solving, we get

$$\frac{1}{\lambda} = \frac{5R}{36} \text{ cm}^{-1}$$

81. Number of electrons in  $ClO_2^-$

$$= 17 + 2 \times 8 + 1 = 34$$

$$\text{Number of electrons in } ClF_2^+$$

$$= 17 + 2 \times 9 - 1 = 34$$

83.  $E = hc/\lambda \quad \dots\dots(1)$

$$E_1 = hc/\lambda_1 \quad \dots\dots(2)$$

$$E_2 = hc/\lambda_2 \quad \dots\dots(3)$$

$$E = E_1 + E_2 = hc (1/\lambda_1 + 1/\lambda_2)$$

$$\frac{1}{\lambda} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$$

$$\frac{1}{(300 \times 10^{-9})} = \frac{1}{(760 \times 10^{-9})} + \frac{1}{\lambda_2}$$

$$1/\lambda_2 = \left( \frac{1}{300} - \frac{1}{760} \right) \times 10^9$$

$$= (0.00333 - 0.00131) \times 10^9$$

$$= 2.02 \times 10^6 \text{ m}^{-1}$$

84.  $\lambda = h/\sqrt{2mE}$

$$= \frac{6.626 \times 10^{-34}}{\sqrt{2 \times 1 \times 0.5}} \text{ m}$$

$$= 6.626 \times 10^{-34} \text{ m}$$

85. According to Heisenberg Uncertainty Principle

$$\Delta p \cdot \Delta x \geq \frac{\hbar}{4\pi}$$

$$m \Delta v \cdot \Delta x \geq \frac{\hbar}{4\pi}$$

$$(m \cdot \Delta v)^2 \geq \frac{\hbar}{4\pi}$$

$$\Delta v \geq \frac{1}{2m} \sqrt{(h/\pi)}$$

86.  $n_1 = 1, n_2 = 4$

$$\text{now use } 1/\lambda = R_H [1/n_1^2 - 1/n_2^2]$$

$$= 1.1 \times 10^7 [1/1^2 - 1/4^2]$$

after solving

$$\lambda = 96.9 \text{ nm.}$$

### 3.52 ■ Atomic Structure

87. For the shortest wave length transition, here  $n_1 = 1$ ,  $n_2 = \infty$

$$\frac{1}{\lambda} = R_H \left[ \frac{1}{1^2} - \frac{1}{\infty^2} \right] \quad \dots(1)$$

and for longest wavelength transition in Paschen series  $n_1 = 3$ ,  $n_2 = 4$

$$\frac{1}{\lambda} = R_H \times 2^2 \left[ \frac{1}{3^2} - \frac{1}{4^2} \right] \quad \dots(2)$$

On considering eq. (1) and (2), we get

$$\lambda = 36X/7$$

88. As we know that  $r_n \propto n^2/Z$ .

For hydrogen  $r = 1$ ,  $Z = 1$ .

For  $\text{Be}^{3+}$ ,  $Z = 4$ ,  $n = 2$  for the same radius.

90. As Q is fluorine and it exists as  $\text{F}_2$ .

92. Both A and B have the valencies 3

So the formula is AB.

93. As Z has 13 electrons, Y has 9 electrons and X has 8 electrons in M shell.

95.  $h\nu_1 = h\nu_0 + \frac{1}{2} m u_1^2 \quad \dots(1)$

$h\nu_2 = h\nu_0 + \frac{1}{2} m u_2^2 \quad \dots(2)$

$$\frac{1}{2} m u_1^2 = \frac{1}{k} (\frac{1}{2} m u_2^2)$$

From equation (1)

$$h\nu_1 = h\nu_0 + \frac{1}{2k} m u_2^2 \quad \dots(3)$$

$$\frac{1}{2} m u_2^2 = k h\nu_1 - kh\nu_0 \quad \dots(4)$$

Bu equation (2) and (4), we get

$$h\nu_2 = h\nu_0 - k h\nu_0 + k h\nu_1$$

$$v_0 (1 - k) = v_2 - kv_1$$

$$\text{So } v_0 = \frac{kv_1 - v_2}{(k-1)}$$

96.  $\frac{h c}{\lambda} = 1 + \Phi \quad \dots(1)$

$$3 \times \frac{h c}{\lambda} = 4 + \Phi \quad \dots(2)$$

From equation (1) and (2), we get

$$\Phi = 0.5 \text{ eV}$$

97. I.E. of  $\text{He}^+ = E \times 2^2$  (as Z for He = 2)

$$\text{I.E. of } \text{Li}^{2+} = E \times 3^2 \text{ (as Z for Li = 3)}$$

Hence

$$\frac{\text{I.E. } (\text{He}^+)}{\text{I.E. } (\text{Li}^{2+})} = \frac{4}{9}$$

$$\text{i.e., I.E. } (\text{Li}^{2+}) = \frac{9}{4} \times \text{I.E. } (\text{He}^+)$$

$$= \frac{9}{4} \times 19.6 \times 10^{-18}$$

$$= 4.41 \times 10^{-17} \text{ J atom}^{-1}$$

99.  $E_n = \frac{13.6}{n^2} \text{ eV}$

For second excited state  $n = 3$ ,

$$E_3 = -\frac{13.6}{9} = -1.51 \text{ eV}$$

102. The lines at the red end suggest Balmer series. These are obtained for the jumps  $n = 2$  from  $n = 3$  and second line from  $n = 4$  and third line from  $n = 5$  i.e.,  $5 \rightarrow 2$ .

103. According to Schrodinger wave equation Probability =  $\psi^2 dV$

Ist orbital is spherically symmetrical

$$V = \frac{4}{3} \pi r^3$$

$$\frac{dV}{dr} = 4 \pi r^2$$

$$\text{So probability} = \psi^2 4\pi r^2 dr$$

105. Any sub-orbit is represented as  $nl$  such that  $n$  is the principle quantum number (in the form of values) and  $l$  is the azimuthal quantum number (its name).

Value of $l < n$ ,	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$
	s	p	d	f	g

value of m:  $-l, -l+1, \dots, 0, +l$

value of s:  $+\frac{1}{2}$  or  $-\frac{1}{2}$

thus for 4f :  $n = 4$ ,  $l = 3$ , m = any value between  $-3$  to  $+3$ .

106. E.C of Cr ( $Z = 24$ ) is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$

so electrons with  $l = 1$  (p), are 12

with  $l = 2$  d, , are 5

107. K.E. =  $\frac{1}{2} mv^2$

$$\text{P.E.} = -Ze^2/r$$

But electrostatic force,

$$\frac{Ze^2}{r^2} = \frac{mv^2}{r}$$

(centrifugal force)

$$\text{P.E.} = -mv^2$$

$$\text{Total energy} = \frac{1}{2} mv^2 - mv^2 = -\frac{1}{2} mv^2$$

So K.E./Total energy = -1.

108. Angular momentum =  $\sqrt{\ell} (\ell + 1) \cdot \frac{h}{2\pi}$

For 2s electron :  $\ell = 0$ ;

$$\text{Angular momentum} = \sqrt{0} \times 1 \cdot \frac{h}{2\pi} = 0$$

For 2p electron :  $\ell = 1$ ;

$$\text{Angular momentum} = \sqrt{1} \times 2 \cdot \frac{h}{2\pi} = \sqrt{2} \cdot \frac{h}{2\pi}$$

109.  $\frac{1}{\lambda} = v_H = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ .

$$= 1.097 \times 10^7 \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right)$$

$$\lambda = \frac{1}{1.097 \times 10^7} \text{ m} = 9.11 \times 10^{-8} \text{ m}$$

$$= 91.1 \times 10^{-9} \text{ m}$$

$$= 91.1 \text{ nm} \quad (1 \text{ nm} = 10^{-9} \text{ m})$$

115.  $E = nhv = \frac{n hc}{\lambda} = n hc \bar{v}$

(as  $\bar{v} = 1/\lambda$ )

$$\text{As } E = 3J$$

$$3 = nhc \bar{v}$$

$$n = \frac{3}{hc \bar{v}} = \frac{3}{hca}$$

116. Radius of the 6<sup>th</sup> orbit =  $6^2 r_0 = 36 r_0$  Circumference =  $2\pi (36 r_0) = 72 \pi r_0$

$$\text{As } n\lambda = 2\pi r_n$$

$$6\lambda = 72 \pi r_0$$

$$\text{So } \lambda = 12 \pi r_0$$

118.  $\Delta E = mc^2$ .

$$\text{For Lyman series, } m_1 c^2 \propto (1/1^2 - 1/2^2)$$

$$\text{For Balmer series, } m_2 c^2 \propto (1/2^2 - 1/3^2)$$

$$m_1/m_2 = 3 \times 36/4 \times 5$$

$$m_1 : m_2 = 27 : 5$$

120. Let 'n' is the principal quantum number of energy level corresponding to energy (X), the principal quantum number of energy level (Y) is  $(n + 3)$  as it emit 6 wavelengths.

So

$$-\frac{13.6 Z^2}{n^2} = X \quad \dots\dots\dots(1)$$

$$-\frac{13.6 Z^2}{(n+3)^2} = Y \quad \dots\dots\dots(2)$$

On diving equation (1) by (2), we get

$$\frac{X}{Y} = \frac{(n+3)^2}{n^2}$$

On solving, we get

$$\sqrt{X/Y} = 1 + 3/n$$

### Multiple Correct Answer Type Questions

125. As an atomic orbital does not describe the trajectory of the electron but represents the probability of the electron in space around the nucleus.

137. They don't have same energy as they have different  $n + l$  values and for hydrogen the energy order of orbital is  $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$ .

### Linked-Comprehension Type Questions

#### Comprehension 1

154. As  $V_n = 2.186 \times 10^8 \times \frac{Z}{n}$  c.m/s

$$1.093 \times 10^8 = 2.186 \times 10^8 \times \frac{1}{n}$$

$$n=2$$

$$\text{Circumference} = 2\pi r_n \quad [\text{as } r_n = 0.529 \times \frac{n_2}{Z}]$$

$$= 2 \times \frac{22}{7} \times 0.529 \times 10^{-10} \times \frac{22}{1}$$

$$= 13.3 \times 10^{-10} \text{ m}$$

$$= 13.3 \text{ \AA}$$

156. Here the number of waves are four so  $n = 4$

$$\text{Hence } E_p = -27 \times \frac{Z_2}{n_2} \text{ ev}$$

$$= -27.2 = -1.7 \text{ ev}$$

### The IIT-JEE Corner

202. These represent two quantum mechanical spin states which have no classical analogues.

205.  $\lambda = h/mv = \frac{6.626 \times 10^{-34}}{200 \times 10^{-3} \times 5}$   
 $= 6.626 \times 10^{-32}$

### 3.54 ■ Atomic Structure

206. As Mass of one electron =  $9.108 \times 10^{-31}$  kg So 1 kg of electrons =  $1/9.108 \times 10^{-31}$

$$= \frac{10^{31}}{9.108 \times 6.022 \times 10^{23}} \text{ mol}$$

$$= \frac{10^{31-23} \text{ mole}}{9.108 \times 6.022} = \frac{10^8}{9.108 \times 6.022} \text{ mol}$$

207. As maximum number of electrons in any orbit, sub orbit or orbital is decided by Pauli's law.

209. Normality of oxalic acid solution (N)

$$W \times 1000/E \cdot V$$

$$= 6.3/63 \times 1000/250 = 0.4 \text{ N}$$

(Acid) (Base)

$$\text{as } N_1 V_1 = N_2 V_2$$

$$\text{so } 0.4 \times 10 = 0.1 \times V_2$$

$$V_2 = \frac{0.4 \times 10}{0.1} = 40 \text{ ml}$$

210. As 24 g of C has maximum moles i.e., two rest have only one mole so it has maximum number of molecules.

### Numericals For Practice

1. The ratio of the speeds of an electron in the first orbit of hydrogen atom to that in the 4<sup>th</sup> orbit of He<sup>+</sup> will be
  - a. 1 : 3
  - b. 2 : 1
  - c. 1 : 2
  - d. 1 : 4
2. The ionization potential for the electron in the ground state of the hydrogen atom is 13.6 eV atom<sup>-1</sup>. What would be the ionization potential for the electron in the first excited state of Li<sup>2+</sup>?
  - a. 34 eV
  - b. 30.6 eV
  - c. 10.26 eV
  - d. 16.80 eV
3. The ratio of first orbits of H, He<sup>+</sup> and Li<sup>2+</sup> is:
  - a. 1 : 2 : 3
  - b. 6 : 3 : 2
  - c. 1 : 1 : 1
  - d. 1 : 4 : 9
4. The ratio of the difference between 2nd and 3rd Bohr's orbit energy to that between 3rd and 4th orbit energy is
  - a. 20/7
  - b. 7/20
  - c. 27/9
  - d. 6/28
5. The distance between 3rd and 2nd orbits in the hydrogen atom is nearly
  - a.  $2.126 \times 10^{-9}$  cm
  - b.  $2.64 \times 10^{-8}$  cm
  - c.  $10.529 \times 10^{-4}$  cm
  - d.  $11.058 \times 10^{-9}$  cm
6. The ratio of velocity of an electron in second orbit of He<sup>+</sup> with the velocity of light is
  - a. 1:9
  - b. 1:237
  - c. 1 : 137
  - d. 2 : 237
7. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition, n = 4 to n = 2 in the He<sup>+</sup> spectrum?

- a. n = 4 to n = 1      b. n = 3 to n = 2**  
**c. n = 3 to n = 1      d. n = 2 to n = 1**
8. Assuming Rydberg constant ( $R_H$ ) to be 109670 cm<sup>-1</sup>, the longest wavelength line in the Lyman series of the hydrogen spectrum is
  - a. 1215 Å
  - b. 1125 Å
  - c. 970 Å
  - d. 940 Å
9. In which transition of He<sup>+</sup> the wave number will be similar to that first line in the Balmer series of hydrogen atom
  - a. 3 → 2
  - b. 6 → 4
  - c. 5 → 4
  - d. 7 → 6
10. The wave number of the first line in the Balmer series of hydrogen atom is 15200 cm<sup>-1</sup> then wave number of first line in Balmer series of Be<sup>3+</sup> is nearly
  - a.  $2.43 \times 10^5$  cm<sup>-1</sup>
  - b.  $10.86 \times 10^4$  cm<sup>-1</sup>
  - c.  $2.43 \times 10^6$  cm<sup>-1</sup>
  - d.  $11.87 \times 10^5$  m<sup>-1</sup>
11. Using the Bohr model, calculate the wavelength of radiant energy associated with the transition of an electron in the hydrogen atom from the n = 4 orbit to the n = 2?
  - a. 5860 Å
  - b. 2430 Å
  - c. 4860 Å
  - d. 9720 Å
12. A 1.0 g projectile is shot from a gun with a velocity of 100 ms<sup>-1</sup>, de Broglie wavelength is
  - a.  $3.63 \times 10^{-35}$  m
  - b.  $6.63 \times 10^{-30}$  m
  - c.  $6.63 \times 10^{-33}$  m
  - d.  $3.63 \times 10^{-32}$  m

- 13.** For silver metal, the threshold frequency  $v_0$  is  $1.12 \times 10^{17}$  Hz. What is the maximum kinetic energy of photoelectrons produced by shining U.V. light of 15.0 Å wavelength on the metal?
- a.  $3.00 \times 10^{17}$  J      b.  $5.8 \times 10^{17}$  J  
c.  $3.9 \times 10^{17}$  J      d.  $2 \times 10^{15}$  J
- 14.** An electron has wavelength 1 Å. The potential by which the electron is accelerated will be
- a. 0.0726 V      b. 0.0505 V  
c. 0.0826 V      d. 50.25 V.
- 15.** Suppose  $10^{-14}$  of light energy is needed by the interior of human eye to see an object. The photons of green light ( $\lambda = 550$  nm) needed to see the object are
- a. 26      b. 280  
c. 28      d. 300
- 16.** The work function for a metal is 4 eV. To emit a photo electron of zero velocity from the surface of the metal, the wavelength of incident light should be
- a. 2500 Å      b. 3100 Å  
c. 5600 Å      d. 1600 Å
- 17.** If the total energy of an electron in a hydrogen like atom in an excited state is -3.4 eV, then the de Broglie wavelength of the electron will be
- a.  $6.6 \times 10^{-10}$       b.  $3.5 \times 10^{-19}$   
c.  $5 \times 10^{-8}$       d.  $9.33 \times 10^{-11}$
- 18.** An electron is moving with a kinetic energy of  $4.55 \times 10^{-25}$  J. What will be the de Broglie wavelength for this electron?
- a.  $7.26 \times 10^{-8}$  m      b.  $3 \times 10^{-6}$  m  
c.  $3 \times 10^{-10}$  m      d.  $7.28 \times 10^{-7}$  m
- 19.** Calculate the number of quanta of radiations of frequency  $4.66 \times 10^{12}$  s<sup>-1</sup> that must be absorbed in order to melt 5 g of ice (the energy required to melt 1 g of ice is 333 J)
- a.  $3.33 \times 10^{18}$       b. 1900  
c.  $5.38 \times 10^{23}$       d.  $30.96 \times 10^{-20}$
- 20.** The uncertainty in the momentum of an electron is  $1.0 \times 10^{-5}$  kg ms<sup>-1</sup>. The uncertainty in its position will be ( $\hbar = 6.62 \times 10^{-34}$  kg m<sup>2</sup> s<sup>-1</sup>)
- a.  $11.05 \times 10^{-29}$  m      b.  $61.06 \times 10^{-26}$  m  
c.  $5.27 \times 10^{-30}$  m      d.  $5.526 \times 10^{-26}$  m
- 21.** Energy equivalent to rest mass of electron is nearly
- a.  $8.19 \times 10^{-14}$  J      b.  $3.6 \times 10^9$  J  
c.  $6.11 \times 10^{-31}$  J      d.  $61.96 \times 10^{-13}$  J
- 22.** The uncertainty in the position of an electron (mass =  $9.1 \times 10^{-28}$  g) moving with a velocity of  $3.0 \times 10^4$  cm s<sup>-1</sup> accurate upto 0.011 % will be
- a. 1.92 cm      b. 7.68 cm  
c. 0.175 cm      d. 3.84 cm
- 23.** Magnetic moment of any ion m<sup>3+</sup> of 3d series is  $\sqrt{35}$  BM. The atomic number of this metal ion is
- a. 25      b. 26  
c. 27      d. 24
- 24.** The radius of hydrogen atom is 0.529 Å and that of proton is  $1.5 \times 10^{-15}$  m. If we assume that both of these pieces are spherical. What fraction of space in atom of hydrogen will be occupied by the nucleus?
- a.  $2.6 \times 10^{-15}$  m      b.  $3.2 \times 10^{-14}$  m  
c.  $2.3 \times 10^{-14}$  m      d.  $9.2 \times 10^{-14}$  m
- 25.** The energy of an  $\alpha$ - particle is  $6.8 \times 10^{-18}$  J. What will be the wavelength associated with it?
- a.  $4.4 \times 10^{-12}$       b.  $1.1 \times 10^{-12}$  M  
c.  $2.2 \times 10^{-8}$  M      d.  $2.2 \times 10^{-12}$  M

**ANSWER KEYS**

Q.	Ans.								
1.	b	2.	b	3.	b	4.	a	5.	b
6.	c	7.	d	8.	a	9.	b	10.	a
11.	c	12.	c	13.	b	14.	c	15.	b
16.	b	17.	a	18.	d	19.	c	20.	c
21.	a	22.	c	23.	b	24.	c	25.	d

## Hints and Explanations

1. Speed of electron in nth orbit,

$$V = 2.19 \times 10^6 Z / n \text{ ms}^{-1}$$

$$\text{Hence } \frac{V_{\text{H}}}{V_{\text{He}^+}} = \frac{Z \text{ H}^n \text{ He}^+}{Z \text{ He}^{+n} \text{ H}}$$

$$= \frac{1 \times 4}{2 \times 1} = \frac{2}{1}$$

i.e.,  $V_{\text{H}} : V_{\text{He}^+} = 2 : 1$

2. As

$$\Delta E = 13.6 Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ eV atom}^{-1}$$

For the ionization of  $\text{Li}^{2+}$  ( $Z = 3$ ) from first excited state,  $n_1 = 2$  and  $n_2 = \infty$

Hence,

$$\begin{aligned} \text{I.E.} &= \Delta E = 13.6 \times 3^2 \left( \frac{1}{2^2} - \frac{1}{\infty^2} \right) \\ &= 30.6 \text{ eV.} \end{aligned}$$

3.  $r = \frac{n^2}{Z} \times 0.529 \text{ \AA}$

$$r_{\text{H}} : r_{\text{He}} : r_{\text{Li}}^{2+}$$

$$1 : \frac{1}{2} : \frac{1}{3}$$

$$6 : 3 : 2j$$

4. As  $E_n = -1312/n^2 \text{ kJ/mole}$

$$\Delta E_{3-2} = -\frac{1312}{9} - \frac{(-1312)}{4}$$

$$= -1312 \left( \frac{1}{9} - \frac{1}{4} \right)$$

$$= \frac{-1312 \times -5}{36}$$

Similarly

$$\Delta E_{4-3} = -1312 \left( \frac{1}{16} - \frac{1}{9} \right)$$

$$= \frac{-1312 \times -7}{16 \times 9}$$

$$\frac{\Delta E_{3-2}}{\Delta E_{4-3}} = \frac{20}{7}.$$

5. As  $r_n = 0.529 \text{ \AA} \times \frac{n^2}{Z}$ .

$$\text{So } r_3 = 0.529 \times 3^2 = 4.761 \text{ \AA}$$

$$r_2 = 0.529 \times 2^2 = 2.116 \text{ \AA}$$

$$\text{Hence } r_3 - r_2 = 4.761 - 2.116 \text{ \AA}$$

$$= 2.6 \text{ \AA}$$

7. For H-like particles

$$\bar{v} = R Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

As for  $\text{He}^+$  spectrum, for Balmer transition

$n = 4$  to  $n = 2$

So

$$\bar{v} = \frac{1}{\lambda} = R Z^2 \left( \frac{1}{2^2} - \frac{1}{4^2} \right) = \frac{3R}{4}$$

Similarly for H-spectrum

$$\bar{v} = \frac{1}{\lambda} = R \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) = \frac{3R}{4}$$

$$\text{i.e., } \frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4} \quad [\text{as } n_1 = 1]$$

On solving, we get

$$n_2 = 2$$

8. Here longest wavelength means smallest wave number. In Lyman series, it is for jump from  $n_2 = 2$  to  $n_1 = 1$ .

$$\bar{v} = 109670 \left( \frac{1}{1^2} - \frac{1}{2^2} \right)$$

$$= 109670 \times \frac{3}{4} = 82252.5 \text{ cm}^{-1}$$

$$\lambda = \frac{1}{\bar{v}} = \frac{1}{82252.5 \text{ cm}^{-1}}.$$

$$= 1215 \times 10^{-8} \text{ cm} = 1215 \text{ \AA}$$

9. As  $E_n = \frac{-E_{1\text{H}}}{n^2}$

$$\text{So } E_3 - E_2 \text{ for H} = \frac{-E_{1\text{H}}}{9} + \frac{E_{1\text{H}}}{4} = \frac{5 E_{1\text{H}}}{36}$$

Similarly

$$E_6 - E_4 \text{ for He}^+ = \frac{-E_{1\text{H}} \times 2^2}{6^2} + \frac{E_{1\text{H}} \times 2^2}{4^2}$$

$$\text{Hence } E_n \text{ He}^+ = \frac{-E_{1\text{H}} \times Z^2}{n^2} + \frac{5E_{1\text{H}}}{36}$$

13. As  $v = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ ms}^{-1}}{15 \times 10^{-10} \text{ m}}$

$$= 2 \times 10^{17} \text{ s}^{-1} \text{ (or Hz)}$$

$$\text{K.E.} = hv - hv_0 = h(v - v_0)$$

$$= 6.626 \times 10^{-34} \times (2 \times 10^{17} - 1.12 \times 10^{17})$$

$$= 5.8 \times 10^{17} \text{ J}$$

14. As  $\lambda = \frac{h}{\sqrt{(2\text{MeV})}}$ .

$$1 \times 10^{-16} = \frac{6.626 \times 10^{-34}}{\sqrt{(2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19} \times V)}}.$$

On solving, we get

$$V = 0.0826 \text{ V}$$

17. As total energy =  $\frac{-e^2}{2 r_n} = -3.4 \text{ eV} = \frac{E_1}{n^2}$   
 So  $n^2 = \frac{-13.6}{-3.4} = 4$

Here  $n = 2$

The velocity in second orbit

$$= \frac{V_1}{2} = \frac{2.18 \times 10^8}{2} \text{ cm sec}^{-1}$$

$$\text{So } \lambda = \frac{h}{mv}.$$

$$= \frac{6.6 \times 10^{-27} \times 2}{9.108 \times 10^{-28} \times 2.18 \times 10^8} \\ = 6.6 \times 10^{-10}$$

18. As  $\lambda = \frac{h}{\sqrt{(2m \text{ K.E.})}}$ .

$$= \frac{6.626 \times 10^{-34}}{\sqrt{(2 \times 9.1 \times 10^{-31} \times 4.55 \times 10^{-25})}} \\ = 7.28 \times 10^{-7} \text{ m}$$

19. As energy required to melt 5g of ice

$$= 5 \times 333 = 1665 \text{ J}$$

As energy of one quantum =  $h\nu$

$$= 6.626 \times 10^{-34} \times 4.66 \times 10^{12}$$

$$= 30.19 \times 10^{-12}$$

20. As  $\Delta x \cdot \Delta p = \frac{h}{4\pi}$ .

$$\text{So } \Delta x = \frac{h}{4\pi \Delta p}.$$

$$= \frac{6.63 \times 10^{-34}}{4 \times 3.143 \times 10^{-5}}.$$

$$= 0.527 \times 10^{-29}$$

$$= 5.27 \times 10^{-30} \text{ m}$$

21. As rest mass of electron ( $m_e$ )

$$= 9.11 \times 10^{-31} \text{ kg}$$

$$\text{As energy (E)} = mc^2$$

$$= 9.11 \times 10^{-31} \times (3 \times 10^8)^2 \text{ J}$$

$$= 81.99 \times 10^{15} \text{ J}$$

$$= 8.19 \times 10^{-14} \text{ J}$$

22. As  $\Delta x \cdot \Delta v = (h/4\pi)$ .

$$\text{Here } \Delta v = \frac{0.011}{100} \times 3 \times 10^4 \text{ ms}^{-1}$$

$$= 3.3 \text{ cm s}^{-1}$$

$$\text{So } \Delta x = \frac{h}{4\pi m \Delta v}.$$

$$= \frac{6.6 \times 10^{-27}}{4 \times 3.143 \times 9.1 \times 10^{-31} \times 3.3}.$$

On solving, we get

$$\Delta x = 0.175 \text{ cm.}$$

24. As  $v = \frac{4}{3} \pi r^3$

$$\text{So nucleus} = \frac{4}{3} \pi (r_n)^3$$

Similarly,

$$v(\text{hydrogen}) = \frac{4}{3} \pi (r_H)^3$$

$$0.529 n = 0.0529 \times 10^{-9} \text{ m}$$

$$\text{So } \frac{v(\text{nucleus})}{v(\text{hydrogen})} = \frac{r_N^3}{r_H^3}$$

$$= (1.5 \times 10^{-15})^3 = 2.3 \times 10^{-44}$$

$$(0.0529 \times 10^{-9})^3$$

25.  $\lambda = \frac{h}{\sqrt{2mE}}$

$$= \frac{6.626 \times 10^{-34}}{\sqrt{6.8 \times 10^{-18} \times 4 \times 1.66 \times 10^{-27}}}$$

$$= 2.2 \times 10^{-12} \text{ m}$$

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## CHAPTER 4

# Energetics

### Chapter Contents

First law of thermodynamics; Internal energy, work and heat, pressure-volume work; enthalpy, Hess's law; Heat of reaction, fusion and vapourization; Second law of thermodynamics; Entropy; Free energy; Criterion of spontaneity and Various levels of multiple-choice questions.

## THERMODYNAMICS

Thermodynamics is the branch of science which deals with the quantitative relationships between different forms of energy. Or, It deals with the energy changes accompanying physical and chemical transformations.

### Main objectives of Thermodynamics

Its main objectives are as follows:

- To decide the feasibility of a given transformation.
- To derive various energy changes and their inter relations.
- To derive laws like—Phase rule, Law of mass action etc.
- Presentation of experimental data in a correct manner.

### Limitations

Its limitations are as follows:

- It is not applicable when substance is present in less amount.
- It gives no explanation of rate of reaction.
- It gives no explanation of system far from equation.
- It does not deal with internal structure of atoms and molecules.

### Terms Related to Thermodynamics System

It is the region or space to be investigated or the origin at which study of pressure, temperature etc., are to be made and which is isolated from rest of the universe with a bounding surface.

## Surroundings

It is region apart from the system which might be in a position to exchange energy and mass with the system.

## Homogeneous and Heterogeneous Systems

### Homogeneous Systems

It is all over uniform that is made of one phase only. Example, pure liquid or pure solid or pure gas present alone.

### Heterogeneous Systems

It is non uniform as it consist of two or more phases. Example, ice and water, solid in contact with a liquid.

### Type of Systems

Systems are divided into three parts:

- Open System:** In such a system, both matter and energy can be exchanged with the surrounding.

Example, Boiling of water in a beaker,

Lime kiln or ice in an open beaker

Zinc granules reacting with dilute HCl to give hydrogen gas is also an example of open system as hydrogen gas escapes and the heat of reaction is transferred to the surroundings.

- Closed System:** In such a system, exchange of energy takes place only with the surroundings.

Example, Heating of liquid in a sealed tube or ice in a closed beaker.

- Isolated System:** In such a system, there is no exchange of matter or energy with the surroundings. Example, Liquid in a sealed thermos flask or ice in thermous flask.

## Macroscopic system and Macroscopic Properties

A system is said to be macroscopic system when it has a large number of molecules, atoms or ions and the properties associated with it are called macroscopic properties.

Example, pressure, volume, temperature, position, density, colour, refractive index, viscosity and surface tension etc.

## State Variables or Functions

The state of a system is fixed by its macroscopic properties if any of the macroscopic property is changed the state of a system also changes so these properties are called state variables.

These determine the state of a system. These are fundamental properties or thermodynamic parameters which depend only upon initial and final states.

Example, Pressure, temperature, volume, mass and composition are the most important state variables. Some other examples are enthalpy, free energy, internal energy, entropy, pressure, volume and number of moles.

### REMEMBER

In case of a single gas composition is not one of the variables as it always remains 100%.

In a closed system having one or more components, mass is not a state variable.

## Properties of System

All macroscopic properties of a system irrespective of the fact whether they are state variable or not are divided into two types:

### 1. Intensive Properties

Such properties remains same on any division in system that is, do not depend upon amount of substance present in the system.

Example, Temperature, pressure, concentration, density, viscosity, surface tension, specific heat, refractive index, pH, EMF of dry cell, vapour pressure dipole moment etc.

### 2. Extensive Properties

Such properties depend upon amount of substance that is, their values are different in the divided system than in the entire system

Example, Mass, volume, energy, work, internal energy, entropy, enthalpy, heat capacity, length.

- An extensive property can be made intensive by specifying it in unit amount of matter.

$$\text{Example, Density } \approx \left( \frac{\text{Mass}}{\text{Volume}} \right)$$

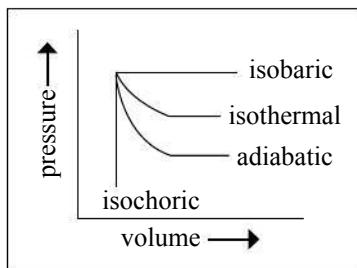
## Thermodynamic Process

It is the path along which a change of state occurs.  
or

It is a path of change of a system from one equilibrium state or another which is usually accompanied by a change in energy or mass.

## Types of Process

Processes are of the following types



### 1. Isothermal Process

Here temperature is kept constant during each step of the process. Example,

$$\Delta T = 0, \Delta E = 0$$

- It is achieved by using a thermostatic control.
- Heat can be absorbed or evolved here that is, can be exchanged with the surroundings.

Example, Freezing, melting, evaporation, condensation.

### 2. Isobaric Process

Here pressure is kept constant ( $\Delta P = 0$ ) during each step of the process.

Example, Expansion of gas in an open system.

- Vaporization and heating of water up to its boiling point occurs at the same atmospheric pressure.

### 3. Isochoric Process

Here volume is kept constant. [ $\Delta V = 0$ ] during each step of the process.

Example, Heating of substance in a closed vessel (system) or non-expanding chamber.

### 4. Adiabatic Process

Here no exchange of heat takes place between the system and the surroundings that is,  $\Delta Q = 0$

- It is achieved by insulating the system or in closed insulated containers (thermos)

### 5. Cyclic Process

- Here the System undergoes a series of changes but finally comes back to initial state.
- $\Delta E = 0, \Delta H = 0$

### Reversible or Quasi-Static Process

It is carried out in such a way that the system remains in a state of equilibrium. All changes occurring at any part of the process will be exactly reversed when change is carried out in the opposite direction.

- It involves slow changes during operation.
- This process may occur in any direction.
- It gives rise to maximum work.
- Here driving force and opposing force differ with each other by a small value.

### Irreversible Process

Here direction of change can not be reversed by small changes in variables. All processes occurring naturally are reversible.

- It involves fast changes during operation.
- It is uni-directional process.
- It gives rise to net work that is  $W_{\text{rev.}} > W_{\text{irr.}}$
- Here, driving and opposing forces differ by a large amount.

### Polytropic Process

$PV^m = \text{constant}$  is known as general or polytropic process.

If  $m = 0$ , the process is at constant pressure.

If  $m = 1$ , the process is at isothermal.

If  $m = \infty$ , the process is constant volume.

If  $m = \gamma$ , the process is at adiabatic.

## 4.4 ■ Energetics

The value of molar specific heat is given as

$$C_m = C_v \frac{(\gamma - m)}{1 - m}$$

### Thermodynamic Equilibrium

A system in which the macroscopic properties do not undergo any change with time is called thermodynamic equilibrium.

If a system is heterogeneous and it is in equilibrium the macroscopic properties in the various phases remain unchanged with time.

**Types:** It is of three types.

#### (i) Mechanical Equilibrium

Here no mechanical work is done by one of the system on another part of the system and it is possible if the pressure remains the same through out the system that is, there is no flow of matter from one part to another.

#### (ii) Thermal Equilibrium

There is no flow of heat from one part to another that is, temperature is constant.

#### (iii) Chemical Equilibrium

There is no change in composition of any part of the system with time.

## HEAT AND WORK

### Heat

Heat is the energy transfer due to difference in temperature. Heat is a form of energy which the system can exchange with the surroundings if they are at different temperatures. The heat flows from higher temperature to lower temperature.

Heat is expressed as 'q'.

Heat absorbed by the system = +q

Heat evolved by the system = -q

Heat is expressed in calorie and the amount of heat required to raise the temperature of one gram of water by 1°C is equal to one calorie.

Now it is also expressed in joule as joule proved that there is a relation between mechanical work done (W) and heat produced (H) as

$$W \propto H$$

$$W = J H$$

Here J = mechanical equivalent of heat

$$J = 4.185 \text{ Joule}$$

### Work

It is the energy transfer due to difference in pressure that is, mode of energy transfer.

$$W = \text{Intensity factor} \times \text{Capacity factor}$$

Here intensity factor is a measure of force responsible for work while capacity factor is a measure of extent for which work is done.

### Types of work

- (i) Mechanical Work (Pressure volume work)  
= Force × Displacement
- (ii) Electrical Work = Potential difference × charge flow  
 $V \times Q = EnF$
- (iii) Expansion Work =  $P \times \Delta V$   
=  $-P_{\text{ext}} \cdot [V_2 - V_1]$   
P = external pressure  
 $\Delta V$  = increase or decrease in volume.
- (iv) Gravitational Work =  $mgh$   
Here m = mass of body,  
g = acceleration due to gravity  
h = height moved.

**Units:** dyne cm or erg (C.G.S.)

Newton meter (joule)

- (i) If the gas expands,  $[V_2 > V_1]$  and work is done by the system and W is negative.
- (ii) If the gas contracts,  $[V_2 < V_1]$  and work is done on the system and W is positive.

### Different Types of Works and the Formulas

- (i) Work done in reversible isothermal process

$$W = -2.303 nRT \log_{10} \frac{V_2}{V_1}$$

$$W = -2.303 nRT \log_{10} \frac{P_1}{P_2}$$

- (ii) Work done in irreversible isothermal process

$$W = -P_{\text{ext.}}(V_2 - V_1)$$

that is,  $W = -P \Delta V$

## Illustrations

1. Calculate the work performed when 2 moles of hydrogen expand isothermally and reversibly at 25°C from 20 to 60 litres.

**Solution**  $W = -2.303 nRT \log_{10} \frac{V_2}{V_1}$

$$= -2.303 \times 2 \times 2 \times 298 \times \log_{10} \frac{60}{20}$$

$$= -1309.7 \text{ Calories}$$

2. Calculate the minimum work necessary to compress 64 g of O<sub>2</sub> from 10 to 5 litres at 300 K. How much heat is evolved in this process?

**Solution**  $W = -2.303 nRT \log_{10} \frac{V_2}{V_1}$

$$W = -2.303 \times \frac{64}{32} \times 2 \times 300 \log \frac{5}{10}$$

$$= -831.8 \text{ calories}$$

$$Q = W = 831.8 \text{ calories}$$

3. Calculate the work done by 10 g of an ideal gas of molecular weight 44 in expanding reversibly and isothermally from a volume of 5 to 10 litre at 300 K.

**Solution**  $W = -2.303 nRT \log_{10} \frac{V_2}{V_1}$

Number of moles of ideal gas  $n = \frac{10 \text{ g}}{44 \text{ g mole}^{-1}}$

$$= \frac{10}{44} \text{ mole}$$

$$R = 1.987 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$T = 300 \text{ K}$$

$$V_2/V_1 = 10/5 = 2$$

On substituting the values, we get

$$W = -2.303 \times \frac{10}{44} \times 1.987 \times 300 \times \log_{10} 2$$

On solving

$$W = -93.93 \text{ cal}$$

## Internal Energy or Intrinsic Energy

The energy stored within a substance is called its internal energy. The absolute value of internal energy cannot be determined.

Or

It is the total energy of a substance depending upon its chemical nature, temperature, pressure, and volume, amount of substrate. It does not depend upon path in which the final state is achieved.

$$E = E_t + E_r + E_v + E_e + E_n + E_{p,E} + E_b$$

$E_t$  = Transitional energy

$E_r$  = Rotational energy

$E_v$  = Vibrational energy

$E_e$  = Electrical energy

$E_n$  = Nuclear energy

$E_{p,E}$  = Potential energy

$E_b$  = Bond energy

The exact measurement of it is not possible so it is determined as  $\Delta E$  as follows:

$$\Delta E = \sum E_p - \sum E_r$$

$$\Delta E = E_f - E_i$$

Here  $E_f$  = final internal energy

$E_i$  = Initial internal energy

$E_p$  = Internal energy of products

$E_r$  = Internal energy of reactants

## Facts about Internal Energy

- It is an extensive property.
- Internal energy is a state property.
- The change in the internal energy does not depend on the path by which the final state is reached.
- Internal energy for an ideal gas a function of temperature only so when temperature is kept constant  $\Delta E$  is zero for an ideal gas.
- For a cyclic process  $\Delta E$  is zero ( $E$  = state function)  
 $E \propto T$
- For an ideal gas it is totally kinetic energy as there is no molecular interaction.

## 4.6 ■ Energetics

- Internal energy for an ideal gas is a function of temperature only hence, when temperature is kept constant it is zero.
- At constant volume (Isochoric)  $Q_v = \Delta E$
- In adiabatic expansion, gas cooled as  $\Delta E$  decreases.
- For exothermic process,  $\Delta E$  is negative as  $E_R > E_p$  but For endothermic process  $\Delta E$  is positive as  $E_R < E_p$ .
- It is determined by using a Bomb calorimeter.

$$\Delta E = \frac{Z \times \Delta T \times m}{w}$$

Z = Heat capacity of Bomb calorimeter

$\Delta T$  = Rise in temperature

w = Weight of substrate (amount)

m = Molar mass of substrate

### Illustrations

4. Calculate the standard internal energy change for the following reaction at 25°C:



$\Delta H^\circ_f$  at 25°C for  $\text{H}_2\text{O}_2(\text{l}) = -188 \text{ kJ mol}^{-1}$

$\text{H}_2\text{O}(\text{l}) = -286 \text{ kJ mole}^{-1}$

**Solution**  $\Delta H^\circ = \sum \Delta H^\circ_f(\text{Products}) - \sum \Delta H^\circ_f(\text{Reactants})$

$$= 2(-286) + 0 - 2(-188)$$

$$= -572 + 376 = -196 \text{ kJ}$$

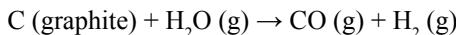
$$\Delta n(\text{g}) = 1 - 0 = 1$$

$$\Delta H^\circ = \Delta E^\circ + \Delta n(\text{g}) RT$$

$$= -196 - 1 \times 8.314 \times 10^{-3} \times 298$$

$$= 198.4775 \text{ kJ}$$

5. Calculate standard internal energy change ( $E^\circ$ ) for the reaction



$\Delta H^\circ_f$  of  $\text{H}_2\text{O}(\text{g}) = -241.8 \text{ kJ mol}^{-1}$

$\Delta H^\circ_f$  of  $\text{CO}(\text{g}) = -110.5 \text{ kJ mol}^{-1}$

**Solution**  $\text{C(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + \text{H}_2(\text{g})$

$$\Delta H^\circ_{\text{reaction}} = \sum \Delta H^\circ_f(\text{Products}) - \sum \Delta H^\circ_f(\text{Reactants})$$

$$= \Delta H^\circ_f(\text{CO}) + \Delta H^\circ_f(\text{H}_2) - [\Delta H^\circ_f(\text{H}_2\text{O}) + \Delta H^\circ_f(\text{C})]$$

$$= 1 \times (-110.5) + (0) - [1 \times (-241.8) + 0]$$

$$= -110.5 + 241.8$$

$$= +131.3 \text{ kJ}$$

$\Delta n = \text{Moles of gaseous products} - \text{Moles of gaseous reactants}$

$$= (1 + 1) - 1$$

$$= 1 \text{ mol}$$

$$\Delta nRT = 1 \times 8.314 \times 298 = 2477.6 \text{ J} = 2.48 \text{ kJ}$$

$$\Delta H = \Delta E + \Delta nRT$$

$$\Delta E = \Delta H - \Delta nRT$$

$$= +131.3 - 2.48 = +128.82 \text{ kJ}$$

### First Law or Law of Conservation of Energy

It was introduced by Helmholtz and according to it “Energy can neither be created nor destroyed but can be converted from one form to another or the total energy of universe is constant”.

It can also be written as:

- Energy of an isolated system must remain constant, although it may be transformed from one form to another.
- Energy in one form, if it disappears will make its appearance in an exactly equivalent in another form.
- When work is transformed into heat or heat into work, the quantity of work is mechanically equivalent to the quantity of heat.
- It is never possible to construct a perpetual motion machine that could produce work without consuming any energy.

Thus if heat is supplied to a system it is never lost but it is partly converted into internal energy and partly in doing work in the system that is,

Heat supplied = Work done by the system

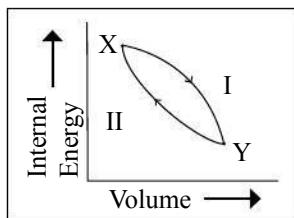
+

Increase in internal energy

So increase in internal energy

= Heat supplied – work done by the system

### Mathematical Formulation of the First Law



If a system absorbs 'q' amount of heat and its state changes from X to Y and this heat is used up.

- On increasing the internal energy of the system

$$\Delta E = E_Y - E_X$$

- In order to do some external work (W) on the surrounding by the system.

From first law we get the relation

$$\Delta E = Q - W \text{ (that is, work done by the system)}$$

$$\delta E = \delta Q - \delta W$$

(Work done by the system or in expansion)

or

$$\Delta E = Q + W \text{ (that is, work done on the system)}$$

$$\delta E = \delta Q + \delta W \text{ or } \delta E = \delta Q + P \delta V$$

(Work done on the system or in compression).

### REMEMBER

+q = Heat absorbed by system

-q = Heat evolved by system

+W = Work done on the system

-W = Work done by the system

### Some Useful Relations Based Upon First Law of Thermodynamics

**For a Reversible Cycle:**  $\Delta E$  or  $\delta E = 0$ ,

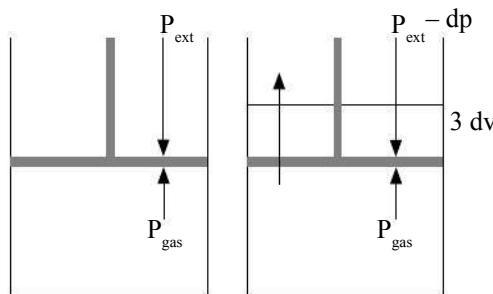
So  $\delta W = \delta q$

$$Q = -W_{\max} = P\Delta V = 2.303nRT \log_{10} \frac{V_2}{V_1} \text{ or } \frac{P_1}{P_2}$$

**For Isochoric Process:**  $\Delta E = Q$  ( $\Delta V = 0$ )

**For Adiabatic Process:**  $\Delta E = W$  (as  $q = 0$ )

### PRESSURE–VOLUME WORK



### Pressure Volume and Work

Let us consider a cylinder fitted with a frictionless and weightless piston having an area of cross section as 'A'. If the external pressure (P) is applied on this piston and the value of P is slightly less than that of the internal pressure of the gas.

When the gas undergoes a little expansion and the piston is pushed out by a small distance  $dx$  the work done by the gas on the piston is given by as

$$dw = \text{force} \times \text{distance} = \text{pressure} \times \text{area} \times \text{distance}$$

$$dw = P.A.dx$$

$$\text{As } A.dx = dV$$

$$dw = P.dV$$

$$dw = P.dV$$

When the volume of the gas changes from  $V_1$  to  $V_2$ , the total work done (W) can be given as

$$W = P \int .dV$$

If we consider the external pressure (P) to be constant than

$$W = P \int dV = P(V_2 - V_1) = P.\Delta V$$

$$W = P.\Delta V$$

### Isothermal irreversible expansion of an ideal gas

When a gas expands against a constant external pressure ( $P_{\text{ext}} = \text{constant}$ ). There is considerable difference between the gas pressure (inside the cylinder) and the external pressure. The temperature does not change during the process.

$$W = - \int_{V_1}^{V_2} P_{\text{ext}} dV$$

$$= -P_{\text{ext}} \int_{V_1}^{V_2} dV$$

$$= -P_{\text{ext}} (V_2 - V_1)$$

$$W = -P_{\text{ext}} \Delta V$$

### Work done in Isothermal reversible expansion of an ideal gas

As a small amount of work done  $\delta W$  on reversible expansion of a gas through a small volume  $dV$  against an external pressure 'P' can be given as

$$\delta W = -PdV$$

So the total work done when the gas expands from initial volume  $V_1$  to final volume  $V_2$  is given as

$$\int_{V_1}^{V_2} PdV$$

As according to ideal gas equation  $PV = nRT$

$$P = \frac{nRT}{V}$$

$$\text{So } W_{\text{rev.}} = \int_{V_1}^{V_2} nRT dV \text{ (as temp. is constant)}$$

$$\text{So } W_{\text{rev.}} = -nRT \ln \frac{V_2}{V_1} = -2.303 nRT \log_{10} \frac{(V_2)}{(V_1)}$$

$$W_{\text{rev.}} = -2.303 nRT \log_{10} \frac{(P_1)}{(P_2)}$$

Here negative sign indicates work of expansion and it is maximum and greater than work in the irreversible process.

As in such a case, temperature is kept constant and internal energy depends only on temperature so it internal energy is constant.

$$\text{So } \Delta E = 0$$

$$\Delta E = q + W$$

$$q = -W$$

Hence, during isothermal expansion, work is done by the system at the expense of heat absorbed.

Here  $\Delta H$  can be found out as follows:

$$\Delta H = \Delta E + \Delta n_g RT$$

As, for isothermal process,  $\Delta E = 0$ ,  $\Delta T = 0$

$$\text{So } \Delta H = 0$$

### Adiabatic Reversible Expansion of An Ideal Gas

As in an adiabatic change there is no transfer of heat that is,  $q = 0$  or  $dq = 0$

$$\text{So } \Delta E = -W$$

$$dE = -dW$$

Suppose only mechanical work of expansion or contraction is made here so  $dW = PdV$

$$\text{As } dE = C_V dT = nC_V dt$$

$$\text{So } C_V dT = -PdV$$

In a system of 1 mole of an ideal gas, for an adiabatic and reversible expansion from temperature  $T_1$  to  $T_2$  and volume  $V_1$  to  $V_2$ , we get

$$C_V dT = \frac{-RT}{V} dV$$

$$\text{or } \frac{dV}{V} = \frac{-C_V}{R} \cdot \frac{dT}{T}$$

$$\text{or } \int \frac{dV}{V} = \frac{-C_V}{R} \int \frac{dT}{T}$$

$$\ln \frac{V_2}{V_1} = \frac{-C_V}{R} \ln \frac{T_2}{T_1} = \frac{C_V}{R} \ln \frac{T_1}{T_2}$$

$$\text{or } \ln \frac{V_2}{V_1} = \ln \left( \frac{T_1}{T_2} \right)^{C_V/R}$$

$$\text{or } (V_1 T_1)^{C_V/R} = (V_2 T_2)^{C_V/R} = K$$

$$C_p - C_v = R$$

$$\ln \frac{V_2}{V_1} = \frac{C_V}{C_p - C_v} \ln \frac{T_1}{T_2}$$

$$\text{or } \frac{C_p - C_v}{C_v} \ln \frac{V_2}{V_1} = \ln \frac{T_1}{T_2}$$

$$\text{or } (\gamma - 1) \ln \frac{V_2}{V_1} = \ln \frac{T_1}{T_2} \text{ (as } \gamma = C_p/C_v)$$

$$\ln \left( \frac{V_2}{V_1} \right)^{\gamma - 1} = \ln \frac{T_1}{T_2}$$

$$\text{or } \left( \frac{V_2}{V_1} \right)^{\gamma - 1} = \left( \frac{T_1}{T_2} \right)$$

$$\text{or } V_2^{\gamma - 1} T_2 = V_1^{\gamma - 1} T_1 = K$$

On substituting T by  $\frac{PV}{R}$  we get

$$\frac{PV}{R} V^{\gamma - 1} = \text{Constant}$$

$$PV^\gamma = R \times \text{Constant} = \text{Constant}$$

Similarly

$$TV^{\gamma-1} = T(RT/P)^{\gamma-1} = \text{Constant}$$

$$T^\gamma P^{1-\gamma} = \text{Constant}$$

### Irreversible Adiabatic Expansion

As in a free expansion the value of external pressure is zero so work done is zero.

that is,  $\Delta E = W = 0$

$$\Delta T = 0, \Delta H = 0$$

During intermediate expansion the volume changes from  $V_1$  to  $V_2$  against external pressure ( $P_{\text{ext}}$ )

$$W = -P_{\text{ext}}(V_2 - V_1) = -P_{\text{ext}} \frac{(RT_2 - RT_1)}{P_2 P_1}$$

$$= -P_{\text{ext}} \frac{(T_2 P_1 - T_1 P_2)}{P_1 P_2} \times R$$

$$W = C_V(T_2 - T_1) = -RP_{\text{ext}} \frac{(T_2 P_1 - T_1 P_2)}{P_1 P_2}$$

### Adiabatic Compression Work

$$W = -C_V T = -C_V(T_2 - T_1) = C_V(T_1 - T_2)$$

As  $T_1, T_2$  are initial and final temperatures respectively

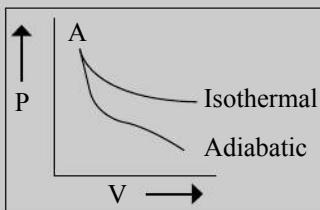
$$\text{For 1 mole of gas } T = \frac{PV}{R}$$

Hence adiabatic work is given as

$$W = C_V \frac{(P_1 V_1 - P_2 V_2)}{R} = \frac{C_V}{R} (P_1 V_1 - P_2 V_2)$$

$$W = \frac{(P_1 V_1 - P_2 V_2)}{(\gamma - 1)}$$

### REMEMBER



### Illustrations

6. Calculate Q, W,  $\Delta E$  and  $\Delta H$  for the isothermal reversible expansion of 1 mole of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K.

- Solution** As in isothermal process as temperature remains constant so both  $\Delta E$  and  $\Delta H$  are zero.

$$\Delta E = 0$$

$$\Delta H = 0$$

According to first law of thermodynamics,

$$\Delta E = W + Q$$

$$0 = W + Q$$

$$Q = -W = -2.303 nRT \log_{10} \frac{P_1}{P_2}$$

$$= -2.303 \times 1 \times 8.314 \times 273 \log_{10} \frac{1}{0.1} \\ = 5227.169 \text{ J}$$

$$= 5.227 \text{ kJ}$$

7. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10 litre to 5 litre. Calculate q, w,  $\Delta E$  and  $\Delta H$  for this process.

( $R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$ ,  $\log 2 = 0.30$ , atomic weight of Ar = 40)

$$\text{Solution } W = -2.303 nRT \log_{10} \frac{V_2}{V_1}$$

$$= -2.303 \times \frac{10}{40} \times 2 \times 300 \log_{10} \frac{5}{10}.$$

$$= 103.635 \text{ cal}$$

$$\Delta E = 0$$

$$q = \Delta E - W$$

$$q = -W = -103.635 \text{ cal}$$

8. A gas expands from a volume of  $3.0 \text{ dm}^3$  to  $5.0 \text{ dm}^3$  against a constant pressure of 3.0 atm. The work done during expansion is used to heat 10.0 mole of water of temperature 290.0 K. Calculate the final temperature of water (Specific heat of water =  $4.184 \text{ JK}^{-1} \text{ g}^{-1}$ ).

## 4.10 ■ Energetics

### Solution

$$\begin{aligned}\text{Work done} &= P \times dV \\ &= 3.0 \times (5.0 - 3.0) \\ &= 6.0 \text{ litre-atm} = 6.0 \times 101.3 \text{ J} \\ &= 607.8 \text{ J}\end{aligned}$$

Let  $\Delta T$  be the change in temperature

$$\begin{aligned}\text{Heat absorbed} &= m \times s \times \Delta T \\ &= 10.0 \times 18 \times 4.184 \times \Delta T \\ P \times dC &= m \times s \times \Delta T \\ \text{or } \Delta T &= \frac{P \times dV}{m \times s} \\ &= \frac{607.8}{10.0 \times 18.0 \times 4.184} \\ &= 0.807\end{aligned}$$

$$\text{Final temperature} = 290 + 0.807 = 290.807 \text{ K}$$

9. Two moles of an ideal gas initially at 300 K and one atm are compressed reversibly to half the initial volume. Find  $q$ ,  $W$ ,  $\Delta E$  and  $\Delta H$  when the process is carried on isothermally.

### Solution

$$W = 2.303 nRT \log_{10} \frac{V_2}{V_1}$$

$$T = 300 \text{ K}$$

$$n = 1$$

$$R = 1.98 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\text{As } V_2 = \frac{1}{2} V_1$$

$$\begin{aligned}W &= 2 \times 2.303 \times 1.98 \times 300 \log_{10} \frac{1}{2} \\ &= -1914.0 \text{ cal}\end{aligned}$$

As the process is being carried on isothermally that is, no change of temperature.

$$\Delta H = 0 \text{ and } \Delta E = 0$$

According to first law of thermodynamics,

$$q = \Delta E + P\Delta V$$

$$q = \Delta E + W$$

$$q = 0 + W$$

$$q = -1914 \text{ cal}$$

$$W = -1914 \text{ cal} \quad \Delta E = 0, \Delta H = 0$$

$$q = -1914 \text{ cal.}$$

10. Find the value of  $Q$ ,  $W$  and  $\Delta E$  for the reversible adiabatic expansion of 1 mole of an ideal gas ( $C_v = 3/2 R$ ) from 5.00 to 25.00 litres at 27°C.

### Solution

For adiabatic process  $Q = 0$ .

$$\Delta E = W = C_v (T_2 - T_1) \quad (\text{for adiabatic})$$

$$T_1 (V_1)^{R/C_v} = T_2 (V_2)^{R/C_v}$$

$$T_2 = T_1 (V_1/V_2)^{R/C_v}$$

$$= 300.0 (5/25)^{2R/3R}$$

$$= 300.0 (5/25)^{2/3}$$

$$T_2 = 102.6 \text{ K}$$

$$\Delta E = W = \frac{3}{2} R (T_2 - T_1)$$

$$= 1.500 \times 1.98 (102.6 - 300)$$

$$\Delta E = -588.4 \text{ cal/mol.}$$

11. One mole of an ideal gas which  $C_v = 3/2 R$  is heated at a constant pressure of 1 atm from 298 K to 373 K. Find  $\Delta H$  and  $\Delta U$ .

### Solution

$$C_v = \frac{3}{2} R$$

$$C_p = C_v + R = \frac{3}{2} R + R = \frac{5}{2} R$$

Heat given at constant pressure =  $m \cdot C_p \Delta T$

$$H \text{ or } q_p = 1 \times \frac{5}{2} R \times (373 - 298)$$

$$\Delta H = 1 \times \frac{5}{2} \times 1.987 \times 75 = 372.56 \text{ cal}$$

Now work done in the process =  $-P\Delta V$

$$W = -P(V_2 - V_1)$$

$$= -P \frac{(nRT_2 - nRT_1)}{P}$$

$$(As PV = nRT)$$

$$= -nR(T_2 - T_1)$$

$$= -1 \times 1.987 \times (373 - 298)$$

$$= -1 \times 1.987 \times 75$$

$$= -149.025 \text{ cal}$$

According to first law of thermodynamics

$$\begin{aligned}\Delta U &= q + W \\ &= 372.56 - 149.05 \\ &= 223.51 \text{ cal.}\end{aligned}$$

12. Calculate  $q$ ,  $W$ ,  $\Delta U$  and  $\Delta H$  for the isothermal reversible expansion of one mole of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K.

### Solution

For isothermal reversible expansion:

$$\begin{aligned}W &= -2.303 nRT \log_{10} \frac{P_1}{P_2} \\ &= -2.303 \times 1 \times 8.314 \times 2.73 \log_{10} \frac{1.0}{0.1}\end{aligned}$$

At constant temperature, for expansion  $\Delta T = 0$ , therefore  $\Delta U = 0$

$$\Delta U = 1 \times C_v \times \Delta T = 0 \quad (\text{for 1 mole})$$

$$\Delta U = q + w$$

$$\text{So } q = -W = 5227.2 \text{ J}$$

At constant temperature,  $P_1 V_1 = P_2 V_2$  or  $PV$  is constant.

$$\text{So } \Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = 0$$

### Limitations of the First Law of Thermodynamics

- It fails to explain why heat cannot be completely converted into work.  
that is,  $W = JH$
- It fails to tell the spontaneity of the process.
- It can establish the relation between  $+q$  and  $-W$  but it puts no restriction regarding the direction of flow of heat.
- This law fails to tell us under what conditions and to what extent it is possible to bring about conversion of one form of energy into the other.
- The first law fails to contradict the non-existence of a 100 per cent efficient heat engine or a refrigerator.
- It fails to explain the expansion of gases in vacuum when  $\Delta E = 0$ ,  $\Delta H = 0$ ,  $W = 0$ .
- It fails to explain the expansion of gases in vacuum when  $\Delta E = 0$ ,  $\Delta H = 0$ ,  $W = 0$ .

### Heat Content or Enthalpy Change or Heat content ( $H$ )

If we deal a process in open vessel (at constant pressure), it becomes essential to use a new thermodynamic function heat enthalpy in place of internal energy. It is defined as "The amount of heat absorbed or evolved by a system at constant pressure". Mathematically, it is the sum of internal energy pressure volume energy.

- It is not a state function.
- It is denoted by  $H$  at constant pressure.
- It is denoted by  $E$  at constant volume.
- Enthalpy of the elements in gaseous, liquid or solid or combined state is taken as zero.

Example,  $C$ ,  $O_2$ ,  $H_2$  etc.

**Relation Between  $\Delta H$  and  $\Delta E$ :** Mathematically, enthalpy change is equal to the sum of internal energy( $E$ )

And pressure volume energy which is given as,

$$H = E + PV$$

The change in enthalpy of a given system is given as:

$$\Delta H = H_2 - H_1$$

$$\text{or } \Delta H = (E_2 + P_2 V_2) - (E_1 + P_1 V_1)$$

$$\Delta H = (E_2 - E_1) + (P_2 V_2 - P_1 V_1)$$

$$\text{or } \Delta H = \Delta E + \Delta(PV)$$

If 'P' is constant

$$\Delta H = \Delta E + P\Delta V$$

$$\text{or } \Delta H = Q$$

Hence the change in enthalpy of the system  $\Delta H$  may be defined as the amount of heat absorbed at constant pressure.

$$\text{As } P\Delta V = \Delta n_g RT$$

$$\text{So } \Delta H = \Delta E + \Delta n_g RT$$

Here  $\Delta H$  = change in enthalpy in constant pressure

$\Delta E$  = change in enthalpy in constant volume.

$\Delta n_g$  = difference in the moles of gaseous reactants and product

## Illustrations

- 13.** The heat liberated on complete combustion of 7.8 g benzene is 327 kJ. This heat has been measured of constant volume and at 27°C. Calculate heat of combustion of benzene at constant pressure at 27°C. ( $R = 8.314 \text{ J/mol/K}$ ).

**Solution**  $\text{C}_6\text{H}_6(\text{l}) + 7\frac{1}{2}\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$

$$\Delta n = 6 - 7\frac{1}{2} = -3/2$$

$$\Delta H = \Delta E - \Delta n RT$$

$$(\Delta E \text{ per mole for benzene} = (327 \times 78)/7.8)$$

$$= -327 \text{ kJ}$$

$$= -3270 \times 10^3 + (-3/2) \times 8.314 \times 300$$

$$= -32737413 = -3273.74 \text{ kJ}$$

- 14.** Calculate the standard internal energy change for the following reaction at 25°C.



$$\Delta H^\circ_f \text{ at } 25^\circ\text{C}$$

$$\text{H}_2\text{O}_2(\text{l}) = -188.0 \text{ kJ mole}^{-1}$$

$$\text{H}_2\text{O}(\text{l}) = -286.0 \text{ kJ mole}^{-1}$$

$$(R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1})$$

**Solution**  $2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$

$$\Delta H^\circ = \Delta H^\circ_f(\text{products}) - \Delta H^\circ_f(\text{reactants})$$

$$= (2 \times 286 + 0.0) - (2 \times -188)$$

$$= -196 \text{ kJ}$$

$$\Delta n = 3 - 2 = 1$$

$$\Delta E^\circ = \Delta H^\circ - \Delta n RT$$

$$= -196 \times 10^3 - 1 \times 8.314 \times 298$$

$$= -193.58 \text{ kJ}$$

## Heat Capacity

The heat capacity of a system is defined as “The quantity of heat required for increasing the temperature of one mole of a system through 1°C”. It is given as follows:

$$C = \frac{\delta q}{dT} \quad \dots \quad (1)$$

### (i) Heat capacity at constant volume

According to first law of thermodynamics,

$$\delta q = dE + PdV \quad \dots \quad (2)$$

On substituting the value of  $\delta q$  in equation (2)

$$C = \frac{dE + PdV}{dT} \quad \dots \quad (3)$$

If volume is constant then

$$C_v = (dE/dT)_v \quad \dots \quad (4)$$

Hence the heat capacity at constant volume of a given system may be defined as the rate of change of internal energy with temperature.

### (ii) Heat capacity at constant pressure

If pressure is constant, equation (3) becomes as follows:

$$C_p = \frac{dE + PdV}{dT}$$

$$\text{or } C_p = (\delta q/dT)_v$$

Hence the heat capacity at constant pressure of a system may be defined as the rate of change of enthalpy with temperature.

- For one mole of a gas  $C_p$  and  $C_v$  are known as molar heat capacities and the difference between them is equal to the work done by one mole of gas in expansion on heating it through 1°C.

At constant pressure work done by the gas

$$= P\Delta V$$

$$\text{For one mole of gas } PV = RT$$

On increasing temperature by 1°C, the volume becomes  $V + \Delta V$

$$\text{Hence } P(V + \Delta V) = R(T + 1)$$

$$\text{or } P\Delta V = R$$

$$\text{that is, } C_p - C_v = P\Delta V = R$$

## Thermochemistry

It deals with the heat changes during chemical reactions. It is called chemical energetics and based on first law of thermodynamics. It is called as chemical energetics and based on first law of thermodynamics.

## Exothermic Reaction

- Heat is evolved here.
- $\Delta H$  is -ve as  $H_p > H_R$
- $\Delta H = H_p - H_R = -ve$  (at constant pressure)

At constant volume,

$$\Delta E = (E_p - E_R) = -ve$$

that is,  $E_p > E_R$

## Endothermic Reaction

- Here heat is absorbed.
- $\Delta H$  or  $\Delta E = +ve$  for endothermic
- $\Delta H = H_p - H_R = +ve$  (at constant pressure as )
- As  $H_p > H_R$  or  $E_p > E_R$
- At constant volume

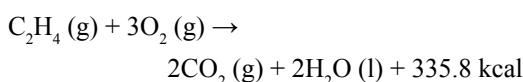
$$\Delta E = (E_p - E_R) = +ve$$

## Heat or Enthalpy of Reaction

It is the change in enthalpy (amount of heat evolved or absorbed) when the number of gm-moles of the substance indicated by a chemical reaction have undergone complete reaction.

- It is determined by water and Bomb calorimeters. Mathematically, it is given as
- $$= \sum H_p - \sum H_R$$
- It can be express by  $[\Delta H]_p$  or  $[\Delta E]_V$  at constant pressure and volume respectively.

Example,



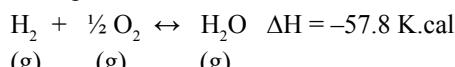
Here 335.8 kcal heat is evolved or 335.8 kcal of internal energy of the system is decreased.

## Factors Effecting Heat of Reaction

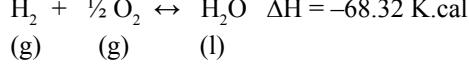
### 1. Nature or Physical State of Reactant and Products

Heat of reaction changes with the change of physical state of the reactants or the products.

Example,



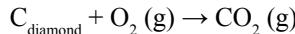
(g) (g) (g)



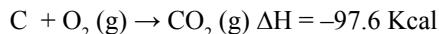
(g) (g) (l)

that is, when steam condenses heat is evolved.

## 2. Allotropic Forms of the Element



$$\Delta H = -94.3 \text{ Kcal}$$



(amorphous)



(d) (amp.)

This Heat is called **Heat of Transition**.

## 3. Enthalpies of Solution

Heat of reaction changes when in one case dry substance react and in another case the solution state of the substance react.

Example,



(g) (g)



(sol) (sol)

## 4. Temperature

The effect of temperature on heat of reaction is given by Kirchoff equation as follows:

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p dT = \Delta C_p \int_{T_1}^{T_2} dT = \Delta C_p \Delta T$$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p$$

$$\Delta E_2 - \Delta E_1 = \int_{T_1}^{T_2} \Delta C_v dT = \Delta C_v \int_{T_1}^{T_2} dT = \Delta C_v \Delta T$$

$$\frac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta C_v$$

**For a Reaction at Constant Pressure or Constant Volume:**

$$\Delta H = \Delta E + \Delta nRT$$

## 4.14 ■ Energetics

$$\Delta H = \Delta E + P\Delta V$$

$$\Delta H = \Delta E + \Delta(PV)$$

\*  $\Delta n$  = number of gaseous product – number of reactant molecules.

### Illustrations

- 15.** A sample of 0.16 g  $\text{CH}_4$  was subjected to combustion at  $27^\circ\text{C}$  in a bomb calorimeter. The temperature of the calorimeter system (including water) was found to rise by  $0.5^\circ\text{C}$ . Calculate the heat of combustion of methane at (i) constant volume (ii) constant pressure. The thermal capacity of calorimeter system is  $17.7 \text{ kJ K}^{-1}$  and  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ .

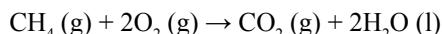
**Solution** Heat of combustion at constant volume,

$\Delta E$  = Heat capacity of calorimeter system  $\times$  rise in

$$\text{temperature} \times \frac{\text{Mol. mass of compound}}{\text{Mass of compound}}$$

$$= 17.7 \times 0.5 \times \frac{16}{0.16} = 885$$

that is,  $\Delta E = -885 \text{ kJ mol}^{-1}$



$$\Delta n = 1 - 3 = -2$$

$$T = 27 + 273 = 300 \text{ K}$$

$$R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta H = \Delta E + \Delta nRT$$

$$= -885 + (-2) \times 8.314 \times 10^{-3} \times 300$$

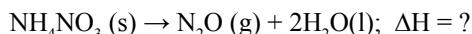
$$= -885 - 4.988$$

$$= -889.988 \text{ kJ mol}^{-1}$$

- 16.** The molar heat of formation of  $\text{NH}_4\text{NO}_3(\text{s})$  is  $-367.54 \text{ kJ}$  and those of  $\text{N}_2\text{O}(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$  are  $81.46$  and  $-285.8 \text{ kJ}$  respectively at  $298 \text{ K}$  and  $1 \text{ atm}$  pressure. Find  $\Delta H$  and  $\Delta U$  of the reaction.



### Solution



$$\Delta H_{\text{Reaction}} = \Delta H_{\text{Products}} - \Delta H_{\text{Reactants}}$$

$$= \Delta H_{\text{N}_2\text{O}} + \Delta H_{\text{H}_2\text{O}} \times 2 - \Delta H_{\text{NH}_4\text{NO}_3}$$

$$\Delta H_{\text{N}_2\text{O}} = +81.46 \text{ kJ}$$

$$\Delta H_{\text{H}_2\text{O}} = -285.8 \text{ kJ}$$

$$\Delta H_{\text{NH}_4\text{NO}_3} = -367.54 \text{ kJ}$$

$$\Delta H_{\text{Reaction}} = +81.46 + 2(-285.8) - (-367.54)$$

$$\Delta H = -122.6 \text{ kJ}$$

$$\Delta H = \Delta U + \Delta nRT$$

$$\text{Here } \Delta n = 1 - 0 = 1$$

$$R = 8.314 \text{ J}$$

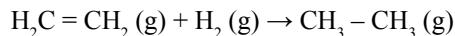
$$T = 298 \text{ K}$$

$$-122.6 \times 10^3 = \Delta U + 1 \times 8.314 \times 298$$

$$\Delta U = -125077 \text{ Joule}$$

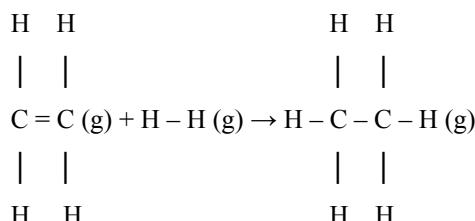
$$= -125.077 \text{ kJ}$$

- 17.** Calculate the enthalpy of the following reaction:



The bond energies of C – H, C – C, C = C and H – H are 99, 83, 147 and 104 kcal respectively.

### Solution



$$\Delta H = ?$$

$\Delta H$  = Sum of bond energies of reactants

– Sum of the bond energies of products

$$= [\Delta H_{\text{C=C}} + 4 \times \Delta H_{\text{C-H}} + \Delta H_{\text{H-H}}]$$

$$- [\Delta H_{\text{C-C}} + 6 \times \Delta H_{\text{C-H}}]$$

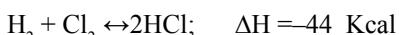
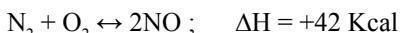
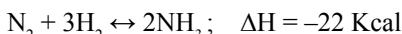
$$= (147 + 4 \times 99 + 104) - (83 + 6 \times 99)$$

$$= -30 \text{ kcal.}$$

### Heat of Formation

The amount of heat evolved or absorbed or change in enthalpy when 1 mole of a substance is obtained from its constituents or free elements.

Example,



■ Heat of formation of  $\text{NH}_3$  is  $-11$  Kcal

Heat of formation of NO is  $+21$  Kcal.

Heat of formation of HCl is  $-22$  Kcal.

■ Heat of formation at  $25^\circ\text{C}$  and 1 atm pressure is called standard heat of formation ( $\Delta H^\circ$ ).

State	Standard State
Solid	Stable crystalline form at a given temperature and 1at pressure.
Liquid	Pure liquid at a given temperature and 1at pressure
Gas	Idea gas at a given temperature and 1at pressure

$$\Delta H^\circ = \sum H^\circ p - \sum H^\circ r$$

Once the value of  $H^\circ$  at  $25^\circ\text{C}$  for any species has been assigned the value of  $H^\circ$  at other temperature

Can be find out by using kirchoff's equation as follows.

$$\frac{T}{298} \int dH^\circ = \frac{T}{298} \int Cp^{\circ} dT$$

$$Ht^\circ - H^\circ = \frac{T}{298} \int Cp^{\circ} dT$$

$$Ht^\circ = H^\circ + \frac{T}{298} \int Cp^{\circ} dT$$

■ Standard heat of formation of free element is taken as zero.

Example, In carbon—graphite form is taken as standard state and in sulphur, monoclinic form is standard state.

■ Heat of formation may be +ve or -ve.

If  $\Delta H$  is -ve compound is exothermic.

If  $\Delta H$  is +ve compound is endothermic.

■ Stability of exothermic compound is more than that of endothermic compound hence, greater the liberated energy greater is the stability of compound.

Example, HF > HCl > HBr > HI

## Illustrations

18. The molar heat of formation of  $\text{NH}_4\text{NO}_3$  (s) is  $-367.5$  kJ and those of  $\text{N}_2\text{O}$  (g) and  $\text{H}_2\text{O}$  (l) are  $+81.46$  kJ and  $-285.78$  kJ respectively at  $25^\circ\text{C}$  and 1 atmospheric pressure. Calculate  $\Delta H$  and  $\Delta E$  for the reaction.



**Solution**  $\Delta H^\circ = \Delta H^\circ_f \text{ (products)} - \Delta H^\circ_f \text{ (reactants)}$

$$= [\Delta H^\circ_f (\text{N}_2\text{O}) + 2 \times \Delta H^\circ_f (\text{H}_2\text{O})] - [\Delta H^\circ_f (\text{NH}_4\text{NO}_3)]$$

$$= 81.46 + 2 \times (-285.78) - (-367.5)$$

$$= 81.46 - 571.56 + 367.5$$

$$= -122.56 \text{ KJ}$$

$$\Delta H = \Delta E + \Delta nRT$$

$$\Delta E = \Delta H - \Delta nRT$$

$$\Delta n = 1$$

$$R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$$

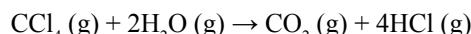
$$T = 298 \text{ K}$$

$$\Delta E = -122.56 - (1) \times (8.314 \times 10^{-3}) \times 298$$

$$= -122.56 - 2.477$$

$$= -125.037 \text{ kJ}$$

19. The standard heats of formation at  $298 \text{ K}$  for  $\text{CCl}_4$  (g),  $\text{H}_2\text{O}$  (g),  $\text{CO}_2$  (g) and  $\text{HCl}$  (g) are  $-25.5$ ,  $-57.8$ ,  $-94.1$  and  $-22.1$  kcal  $\text{mol}^{-1}$  respectively, Calculate  $\Delta H_{298 \text{ K}}^\circ$  for the reaction



**Solution**  $\Delta H_{(\text{reaction})} = \sum \text{Heat of formation of products}$

$- \sum \text{Heat of formation of reactants}$

$$= [\Delta H_f (\text{CO}_2) + 4 \Delta H_f (\text{HCl})] - [\Delta H_f (\text{CCl}_4) + 2\Delta H_f (\text{H}_2\text{O})]$$

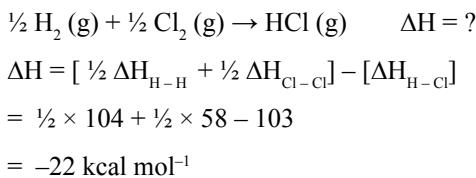
$$= [-94.1 + 4 \times (-22.1)] - [-25.5 + 2 \times (-57.8)]$$

$$= -41.4 \text{ kcal.}$$

20. The bond dissociation energies of gaseous  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$  are  $104$ ,  $58$  and  $103$  kcal  $\text{mol}^{-1}$  respectively. Calculate the enthalpy of formation of  $\text{HCl}$  (g).

## 4.16 ■ Energetics

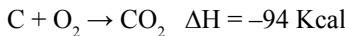
### Solution Reaction



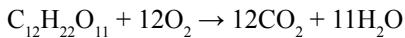
### Heat of Combustion

- It is change in enthalpy when one mole of a substance is completely oxidized or combusted or burnt.
- $\Delta H$  is -ve here as heat is always evolved here that is, exothermic process.
- Heat of combustion is useful in calculating calorific value of food and fuels.
- It is also useful in confirming structure of organic molecules having C,H,O,N etc.
- Enthalpy change by combustion of 1 gm solid or 1 gm liquid or 1 cc gas is called calorific value.

$$C.V = \frac{\text{Heat of combustion}}{\text{Molecular wt.}}$$



$$C.V = -\frac{94}{12} = -7.83 \text{ Kcal}$$



$$\Delta H = -1349 \text{ Kcal}$$

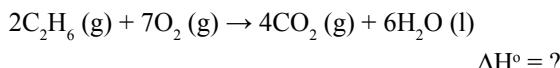
$$C.V = -\frac{1349}{342} = 3.94$$

$$\Delta H(\text{heat of reaction}) = -\sum \Delta H_f^{\circ} - \sum H_f^{\circ}$$

### Illustrations

21. The standard molar heats of formation of ethane, carbon dioxide and liquid water are -21.1, -94.1 and -68.3 kcal respectively. Calculate the standard molar heat of combustion of ethane.

### Solution Reaction for combustion of ethane is as follows.



This reaction involves 2 moles of  $\text{C}_2\text{H}_6$ :

$$\begin{aligned} \text{Heat of combustion of ethane} &= \frac{\Delta H^{\circ}}{2} \\ \Delta H^{\circ} &= \Delta H_f^{\circ}(\text{products}) - \Delta H_f^{\circ}(\text{reactants}) \\ &= [4 \Delta H_f^{\circ}(\text{CO}_2) + 6 \Delta H_f^{\circ}(\text{H}_2\text{O})] - [2 \Delta H_f^{\circ}(\text{C}_2\text{H}_6) + 7 \Delta H_f^{\circ}(\text{O}_2)] \\ &= [4 \times (-94.1) + 6 \times (-68.3)] - [2 \times (-21.1) + 7 \times 0] \\ &= -376.4 - 409.8 + 42.2 \\ &= -744.0 \text{ kcal} \end{aligned}$$

$$\begin{aligned} \Delta H/2 &= \text{Heat of combustion of ethane} \\ &= -\frac{744.0}{2} \\ &= -372.0 \text{ kcal} \end{aligned}$$

22. An intimate mixture of ferric oxide and aluminium is used as solid fuel in rockets. Find the fuel value per  $\text{cm}^3$  of the mixture. Heat of formation and densities are as follows:

$$H_f(\text{Al}_2\text{O}_3) = -399 \text{ kcal mol}^{-1}$$

$$H_f(\text{Fe}_2\text{O}_3) = -199 \text{ kcal mol}^{-1}$$

$$\text{Density of Al} = 2.7 \text{ g/cm}^3$$

$$\text{Density of Fe}_2\text{O}_3 = 5.2 \text{ g/cm}^3$$

### Solution Reaction



$$\Delta H = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$$

$$= [\Delta H_f(\text{Al}_2\text{O}_3) + 2 \Delta H_f(\text{Fe})] - [2 \Delta H_f(\text{Al}) + \Delta H_f(\text{Fe}_2\text{O}_3)]$$

$$= [-399 + 2 \times 0] - [2 \times 0 + (-199)]$$

$$= -399 + 199 = -200 \text{ kcal}$$

$$\text{Atomic mass of Al} = 27$$

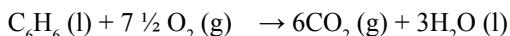
$$\text{Molecular mass of Fe}_2\text{O}_3 = 160$$

$$\begin{aligned} \text{Volume of reactants} &= \frac{160}{5.2} + 2 \times \frac{27}{2.7} \\ &= 50.77 \text{ cm}^3 \end{aligned}$$

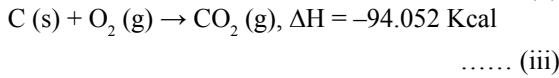
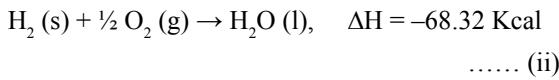
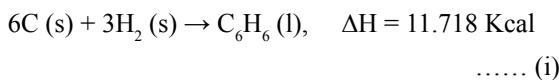
$$\text{Fuel value per } \text{cm}^3 = \frac{200}{50.77} = 3.92 \text{ kcal}$$

23. Given the heats of formation of benzene (liquid), water and carbon dioxide gas at 298 K as 11.718, -68.32 and -94.052 Kcal. Calculate the heat of combustion of liquid benzene at 298 K.

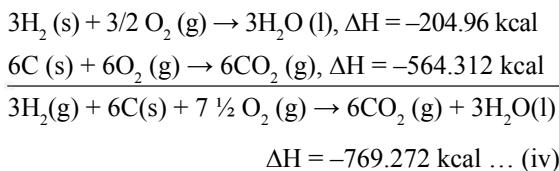
**Solution** The reaction is as follows:



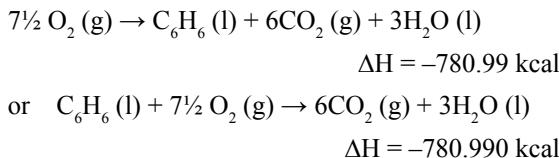
The given data:



Multiply reaction (ii) by 3 and reaction (iii) by 6, and then add reaction (ii) and (iii)



Subtract reaction (i) from reaction (iv)

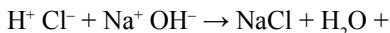


Therefore heat of combustion of benzene is—  
780.99 kcal.

## Heat of Neutralization

It is enthalpy change during neutralization of 1 gm mole of an acid and base. It is also heat of formation of water.

Example,



13.7 Kcal/mole or 57.3 kJ/mole



or 57.3 kJ/mole

$\Delta H = -13.7 \text{ Kcal}$  or  $-57.3 \text{ kJ/mole}$

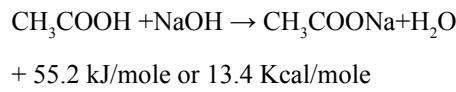
■ It is always exothermic  $\Delta H = -ve$

■ Heat of neutralization of strong acid and strong base is always 13.7 Kcal/mole or 57.3 kJ/mole

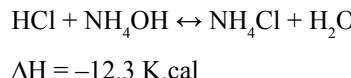
■ It is independent of nature of strong acid or strong base.

■ If one electrolyte is weak than  $\Delta H$  will be less than  $-13.7 \text{ Kcal}$  as some amount of heat will be absorbed in ionization of weak electrolyte.

Example,

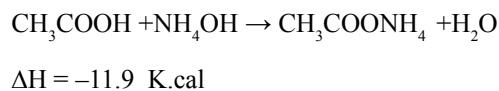
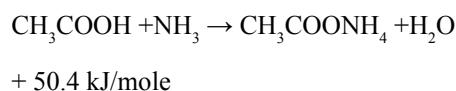


Example,



i.e., heat of ionization of  $\text{CH}_3\text{COOH}$  is 0.3 Kcal or 1.9 kJ/mole

■ If both electrolytes are weak then



■ In case of HF,  $\Delta H$  is more due to more hydration of  $\text{F}^-$  ions.

## Measurement

In laboratory it is measured by using polythene on polystyrene bottles as follows.

Here 10 ml of each of acid and alkali having same normality are taken in separate bottles and temperature is noted at regular intervals. When constant temperature is achieved, the alkali solution is added to the acid solution. The mixture is stirred and the highest temperature is noted.

Suppose  $T_1$  and  $T_2$  are initial and final temperatures here then

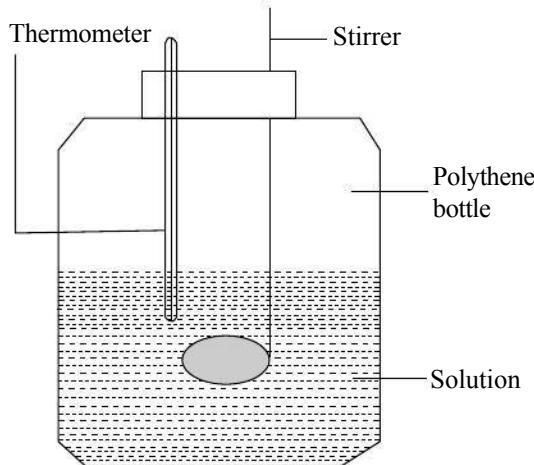
$$\text{Rise in temperature} = (T_2 - T_1) \text{ K}$$

Here specific heat capacity of the solution is assumed to be the same as that of water while heat capacity can be ignored as it is quite less than that of solution.

$$Q = ms(T_2 - T_1)$$

$$\text{Hence, } \Delta H = \frac{Q}{100} \times 1000 \times \frac{1}{N}$$

## 4.18 ■ Energetics

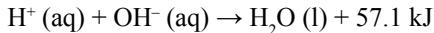


Neu.

Here,  $Q$  = Heat change during the process  
 $S$  = Specific heat of solution  
 $M$  = Mass of solution  
 $N$  = Normality of acid/base.

### Illustrations

24. The heat of neutralization is due to the following reaction:



Calculate the amount of heat evolved when

- (i) 0.25 mole of  $\text{H}_2\text{SO}_4$  is neutralized by 0.5 mole of NaOH and
- (ii) 0.25 mole of  $\text{CH}_3\text{COOH}$  is mixed with 0.25 mole of NaOH, assuming 0.25 J of heat is utilized in the ionization of  $\text{CH}_3\text{COOH}$ .

### Solution

- (i) As 1 mole of  $\text{H}_2\text{SO}_4$  = 2 mole  $\text{H}^+$   
 $\text{So } 0.25 \text{ mole of } \text{H}_2\text{SO}_4 = 0.25 \times 2 \text{ mole } \text{H}^+$   
 $= 0.50 \text{ mole } \text{H}^+$   
 $\text{As } 1 \text{ mole of } \text{H}^+ + 1 \text{ mole } \text{OH}^- = 57.1 \text{ kJ}$   
 $\text{So } 0.50 \text{ mole } \text{H}^+ + 0.50 \text{ mole } \text{OH}^-$   
 $= 57.1 \times 0.5 \text{ kJ} = 28.55 \text{ kJ}$
- (ii) 1 mole  $\text{CH}_3\text{COOH}$  = 1 mole  $\text{H}^+$   
 $0.25 \text{ mole } \text{CH}_3\text{COOH} = 0.25 \text{ mole } \text{H}^+$   
 $(\text{If it is completely ionized})$

Assuming the complete ionization of  $\text{CH}_3\text{COOH}$ , we get

0.25 mole of  $\text{CH}_3\text{COOH} + 0.25 \text{ mole NaOH}$  gives  $0.25 \times 57.1 \text{ kJ}$

Heat expected = 16.27

But the actual heat obtained

$$= 16.27 - \text{heat used in the ionization}$$

$$= 16.27 - 0.25$$

$$= 16.02 \text{ kJ}$$

25. Calculate the heat of neutralization from the following data, 200 ml of 1 M HCl is mixed with 400 ml of 0.5 M NaOH. The temperature rise in calorimeter was found to be  $4.4^\circ\text{C}$ . Water equivalent of calorimeter is 12 g and specific heat is cal/ml/degree for solution.

**Solution** The heat produced ( $\Delta H_1$ ) during neutralization of 200 Meq. of NaOH and HCl each (Meq. =  $N \times V$ ) is taken up by calorimeter and solution in it.

$\Delta H_1$  = Heat taken up calorimeter and solution in it.

$$\Delta H_1 = m_1 S_1 \Delta T + m_2 S_2 \Delta T = 12$$

$$\text{Total solution} = (200 + 400) \text{ ml} = 2692.8 \text{ cal}$$

As neutralization of 200 Meq. gives heat

$$= -2692.8 \text{ cal}$$

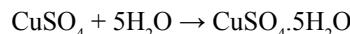
So neutralization of 1000 Meq. gives heat

$$= -2692 \times 5 = -13464 \text{ cal}$$

$$= -13.464 \text{ kcal}$$

### Heat of Hydration

The enthalpy change during hydration of one gm mole substance is called heat of hydration.



+ 78.21 kJ/mole

or 18.7 Kcal/mole

$$\Delta H = -18.7 \text{ K.cal/mole}$$

- It is exothermic mostly

$$H_{\text{sol}} = \Delta H_{\text{hyd}} : \text{Lattice energy}$$

- If  $\Delta H_H > \text{L.E.}$ : solute dissolve in  $\text{H}_2\text{O}$

- $\Delta H_H < L.E.$ : solute does not dissolve in  $H_2O$
- $\Delta H \approx L.E.$ : solute is in equilibrium with solvent in  $H_2O$

## Bond Energy

It may be defined as, “The quantity of heat evolved when a bond is formed between two free atoms in a gaseous state to form a molecular product in a gaseous state”. It is also known as enthalpy of formation of the bond.

Or

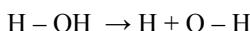
It may also be define as, “The average quantity of heat required to break (dissociate) bonds of that type present in one mole of the compound”.

Example,



The average bond energy per mole of C – H bond =

$$\frac{-398}{4} = -99.5 \text{ Kcal}$$



$$\Delta H = 497.8 \text{ Kj/m}$$

$$(B.E.)_{AV} = \frac{497.8 + 428.5}{2} = 463.15 \text{ Kj/m}$$

When a reaction is carried out in the gas phase at constant pressure, then enthalpy of the reaction can be given as

$$\Delta H = \sum B.E_R - \sum B.E_p$$

$\Delta H$  = (Energy needed to break the bonds in the molecules of the reactants) – (Energy released when bonds in the molecules of the products are formed).

Example, In the case of formation of  $HCl(g)$  from  $H_2(g)$  and  $Cl_2(g)$ ,  $\Delta H = -185 \text{ kJ/mol}$

$$E_{H-H} = 437 \text{ kJ}$$

$$E_{C-Cl} = 244 \text{ kJ}$$

$$E_{H-Cl} = 433 \text{ kJ}$$

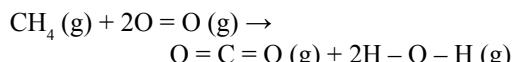
$$So \quad \Delta H = E_{H-H} + E_{C-Cl} - (2E_{H-Cl})$$

$$= 437 + 244 - (2 \times 433)$$

$$= -185 \text{ kJ}$$

## Illustrations

26. Calculate the enthalpy of combustion (enthalpy change) of the given reaction:



From the following B.E. data.

$$BE \text{ of } C-H = 414 \text{ kJ/mol}$$

$$BE \text{ of } C=O = 741 \text{ kJ/mol}$$

$$BE \text{ of } O=O = 395 \text{ kJ/mol}$$

$$BE \text{ of } O-H = 464 \text{ kJ/mol}$$

**Solution**  $\sum(B.E.)_{\text{reactants}}$

$$= 4 \times BE \text{ of } C-H + 2 \times BE \text{ of } O=O$$

$$= 4 \times 414 + 2 \times 395$$

$$= 1656 + 790 = 2446 \text{ kJ}$$

(B.E.) products

$$= 2 \times BE \text{ of } C=O + 2 \times (2 \times BE \text{ of } O-H)$$

$$= 2 \times 741 + 4 \times 1856$$

$$= 3338 \text{ kJ}$$

$$\Delta H = (\sum B.R.)_R - (\sum B.E)_P$$

$$= 2446 - 3338$$

$$= -892 \text{ kJ}$$

27. Calculate the resonance energy of  $N_2O$  from the following data:

$$\Delta H_f^o \text{ of } N_2O = 82 \text{ kJ mol}^{-1}$$

Bond energy of  $N \equiv N$ ,  $N=N$ ,  $O=O$  and  $N=O$  bonds is 946, 418, 498 and 607  $\text{kJ mol}^{-1}$  respectively.

**Solution**  $N \equiv N(g) + \frac{1}{2}(O=O) \rightarrow N=N=O(g)$

$$\Delta H_f(N_2O) = [\Delta H(N \equiv N) + \frac{1}{2}\Delta H(O=O)]$$

$$- [\Delta H(N=O) + \Delta H(N=N)]$$

$$= (946 + \frac{1}{2} \times 498) - (607 + 418)$$

$$= 946 + 249 - 607 - 418$$

$$= 1195 - 1025$$

$$= 170 \text{ kJ mol}^{-1}$$

## 4.20 ■ Energetics

Resonance energy = Observed heat of formation

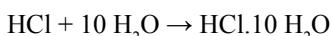
~ Calculated heat of formation

$$= 82 \sim 170$$

$$= 88 \text{ kJ mol}^{-1}$$

### Heat of Dilution

It is change in enthalpy when solution containing one mol of solute is diluted from one concentration to another concentration. Its value depends upon the concentration of solution and on the amount of the solvent added.



$$\Delta H = -69 \text{ KJ /M.}$$

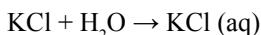
### Heat of Solution

It is change in enthalpy when one mole of a solute is dissolved in excess of solvent.

■  $\Delta H = +ve$  for (hydrated salts)

■  $\Delta H = -ve$  for (anhydrous salts)

Example,



$$\Delta H = -18.6 \text{ KJ/Mole}$$



$$\Delta H = -20.2 \text{ K.Cal.}$$

### Heat of Fusion

It is change in enthalpy in converting one mole of solid into the liquid state at its melting point. It is equal to latent heat of fusion per gram multiplied by the molar mass. It is always positive as heat is needed to overcome the intermolecular forces between constituents particles of solid.

Example, Heat of fusion of  $\text{H}_2\text{O}$



$$(s) \quad (l) \quad = 1.44 \text{ K.Cal.}$$

### Heat of Vaporization

It is the change in enthalpy in converting 1 mole of liquid into the gaseous state at its boiling point

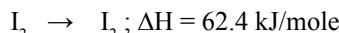
Example,



$$(l) \quad (g) \quad = 10.5 \text{ K.cal.}$$

### Heat of Sublimation

It is the change in enthalpy in converting one mole of a solid directly into vapour at a temperature below its melting point.



$$(s) \quad (g) \quad = 14.9 \text{ K.cal /mole}$$

$$\blacksquare \Delta H_{\text{sub}} = \Delta H_{\text{vap}} + \Delta H_{\text{fus}}$$

### Heat of Atomization

It is the enthalpy change (heat required) when bonds of one mole of a substance are broken down completely to obtain atoms in the gaseous phase (isolated) or it is the enthalpy change when one mole of atoms in the gas phase is formed from the corresponding element in its standard state.

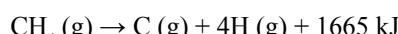
In case of diatomic molecules it is also called bond dissociation enthalpy.

It is denoted by  $\Delta H_a$  or  $\Delta H^*$ .

Example,



$$\Delta H = +435 \text{ kJ/mol}$$



$$\Delta H = +1665 \text{ kJ/mol}$$

### Enthalpy of Dissociation or Ionization

It is defined as, “The quantity of heat absorbed when one mole of a substance is completely dissociated into its ions”. Example,

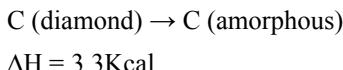


### Phase Transition and Transition Energy

■ The change of matter from one state (solid, liquid or gas) to another state is called Phase Transition.

■ Such changes occur at definite temperatures such as melting point (solid to liquid), boiling point (liquid to vapours) etc., and are accompanied by absorption or evolution of heat. The enthalpy change during such phase transitions is called heat of transition or transition energy.

Example,



## Illustrations

28. Calculate the amount of heat needed to convert 20 g of ice at 0°C to steam at 100°C. If specific heat of water is 1 cal/g, heat of fusion is 80 cal/g and heat of vapourisation is 540 cal/g.

### Solution

$$\begin{aligned}\Delta H_{\text{total}} &= \Delta H_{\text{fus}} + \Delta H_{\text{heat}} + \Delta H_{\text{vap}} \\ &= (20 \times 80) + (20 \times 1 \times 100) + (20 \times 540) \\ &= 1600 + 2000 + 10800 \\ &= 14400 \text{ cal.} = 14.4 \text{ kcal}\end{aligned}$$

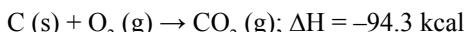
## Law's of Thermochemistry

### Lavosier and Laplace Law

The heat which is required to break a compound into its element is equal to the heat evolved during its formation.

$$\Delta H_D = -\Delta H_f$$

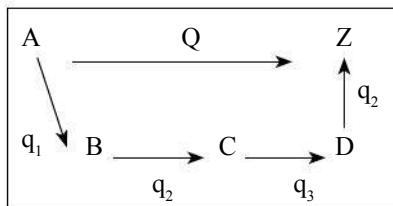
Example,



### Hess's Law

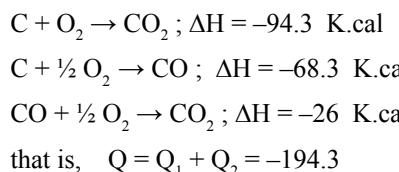
This rule is a consequence of first Law of Thermodynamics and according to it,

"The enthalpy change for a process is independent of path or way of a process. The enthalpy change ( $\Delta H$  or  $\Delta E$ ) for any physical or chemical process remains same whether process is carried out in one step or in many steps."



$$Q = q_1 + q_2 + q_3 + q_4 \dots \dots$$

Example,



Hence it proves that

- $\Delta H$  or  $\Delta E$  is not proportional to path or way of reaction
- $\Delta H$  or  $\Delta E$  is a state function which depends only on initial and final state (first law of thermodynamics)

### Applications Hess Law

It has the following applications:

1. It helps in finding enthalpy changes for those reactions also which are experimentally not possible.
2. It also helps in finding  $\Delta H_{\text{formation}}$ ,  $\Delta H_{\text{combustion}}$  etc.
3. For the determination of resonance energy and lattice energy.
4. For the determination of enthalpies of reactions occurring very slowly.

### Second Law of Thermodynamics

It is not possible to convert heat into work without compensation.

- Work can always be converted into heat but the conversion of heat into work does not take place under all conditions.
- It is impossible to construct a machine that is able to convey heat by a cyclic process from a colder to a hotter body unless work is done on the machine by some outside agency (Clausius statement).
- The heat of the coldest body among those participating in a cyclic process cannot serve as a source of work (Thomson statement).
- It is impossible by means of inanimate material agency to derive mechanical work or effort from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects (Kelvin-Planck statement).
- Nature tends to pass from a less probable to more probable state (Ludwig Boltzmann statement).

## 4.22 ■ Energetics

- Whenever a spontaneous process takes place it is accompanied by an increase in the total entropy of the universe.

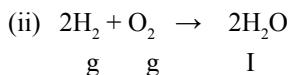
### Spontaneous Process

It is defined as one that proceeds on its own without any outside influence. Its reverse is always non spontaneous which occurs in presence of some continues external influence. Or

The chemical or physical process which occurs in a particular set of conditions either of its own or after proper initiation is known as spontaneous process.

Example,

(i) All natural processes



Formation of water is spontaneous however its decomposition is not spontaneous as it's possible by applying electrical energy for electrolysis.

- Spontaneous Process always occur with the decrease in energy and, increase in disorder (Entropy) and decrease of free energy.

Spontaneous changes which take place by themselves	Spontaneous changes which take place in initiation
Dissolution of $\text{KNO}_3$ in water	Lighting of a candle
Evaporation of water	Decomposition of calcium carbonate .
Flow of heat energy from higher temperature to lower temperature.	Combination of $\text{H}_2$ and $\text{O}_2$ to form water.
Flow of water from higher level to lower level.	Combustion of methane gas.

Dissolution of $\text{KNO}_3$ in water	Lighting of a candle
Evaporation of water	Decomposition of calcium carbonate .
Flow of heat energy from higher temperature to lower temperature.	Combination of $\text{H}_2$ and $\text{O}_2$ to form water.
Flow of water from higher level to lower level.	Combustion of methane gas.

## ENTROPY

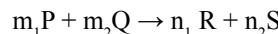
It is a thermodynamic state quantity which is used to measure disorder or randomness of the molecules in a system. The disorder or randomness in a system is measured in terms of entropy (S). The absolute value of 'S' is not determined so mostly change in entropy  $\Delta S$  is measured.

### Randomness & Entropy

It is a state function which depends only on the initial and final state of the system that is, it is independent of the path used in going from the initial to final state.

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

For a general chemical reaction at 298K and 1 atm:



$$\Delta S^\circ = [ (n_1 S^\circ_{\text{R}} + n_2 S^\circ_{\text{S}}) - (m_1 S^\circ_{\text{P}} + m_2 S^\circ_{\text{Q}}) ]$$

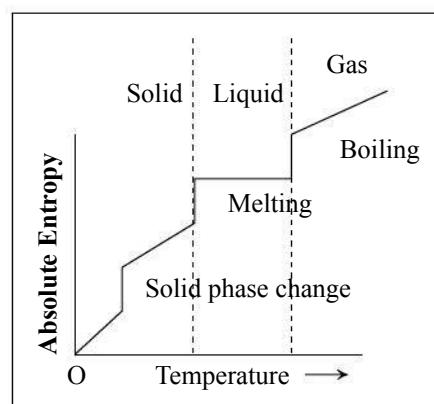
$$\Delta S^\circ = \sum S^\circ_{\text{P}} - \sum S^\circ_{\text{R}}$$

- It is an extensive property and a state function which depends on state variables like T, P, V and n which govern the state of a system.

### Entropy and Temperature

Entropy increases with the increase of temperature as it is associated with the molecular motion which increases with the increase of temperature due to increase in the average kinetic energy of the molecules.

The entropy of a perfectly ordered Crystalline substance is taken as zero at Zero Kelvin (0K). It is third law of Thermodynamics. However in case of  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{LO}$ , Solid  $\text{Cl}_2$  etc. the value of entropy is not found to be zero at 0 Kelvin also.



### Mathematical Definition of Entropy

For a reversible isothermal process, Clausius defined it as the integral of all the terms involving heat exchange (q) divided by the absolute temperature T.

$$ds = \int \frac{q_{\text{rev}}}{T}$$

OR

$$\Delta S = \frac{q_{rev}}{T}$$

Unit:  $J K^{-1} mol^{-1}$

Here  $mol^{-1}$  is also used as entropy being an extensive property depends upon the mass of substance.

### Entropy Changes in Processes

- During isothermal reversible expansion of an ideal gas

As for a reversible path  $\Delta E = 0$

$$So q_{rev} = -W_{rev} = -2.303 \frac{nR}{T} \log_{10} \frac{V_2}{V_1}$$

$$Hence, \Delta S = 2.303 nR \log_{10} \frac{V_2}{V_1}$$

$$\Delta S = 2.303 nR \log_{10} \frac{(P_1)}{(P_2)}$$

- During adiabatic reversible expansion

As  $q = 0$ , so  $\Delta S = 0$

#### 3. Isobaric process:

$$\Delta S = 2.303 n C_p \log_{10} \frac{(T_2)}{(T_1)} \text{ or } \frac{(V_2)}{(V_1)}$$

#### 4. Isochoric process:

$$\Delta S = 2.303 n C_v \log_{10} \frac{(T_2)}{(T_1)} \text{ or } \frac{(P_2)}{(P_1)}$$

#### 5. Entropy change in irreversible processes:

Suppose in a system at higher temperature  $T_1$  and its surroundings at lower temperature  $T_2$ . ‘q’ amount of heat goes irreversibly from the system to the surroundings.

$$\Delta S_{system} = -\frac{q}{T_1}$$

$$\Delta S_{surroundings} = +\frac{q}{T_2}$$

$$\Delta S_{process} = \Delta S_{system} + \Delta S_{surroundings}$$

$$= -\frac{q}{T_1} + \frac{q}{T_2} = q \frac{[T_1 - T_2]}{T_1 T_2}$$

But  $T_1 > T_2$

So  $T_1 - T_2 = +ve$

$$\Delta S_{process} > 0$$

So entropy increases in an irreversible process like conduction radiation etc.

#### 6. Entropy changes during phase transition:

$$\Delta S = S_2 - S_1 = \frac{q_{rev.}}{T} = \frac{\Delta H}{T}$$

##### For fusion

Solid  $\rightleftharpoons$  Liquid

$\Delta H$  = Heat of fusion [Heat required to convert one mole of a solid at constant temperature (melting point) and constant pressure into liquid keeping solid and liquid]

$$\Delta S_{fusion} = S_{liquid} - S_{solid}$$

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{fusion \text{ or M.P.}}}$$

$\Delta H_{fusion}$  = Latent heat of fusion

##### For Vapourization

Liquid  $\rightleftharpoons$  Vapour

$$\Delta S_{vap.} = S_{vapour} - S_{liquid}$$

$$\Delta S_{vap.} = \frac{\Delta H_{vap.}}{T_{vap \text{ or B.P.}}}$$

$\Delta H_{vap.}$  = Latent heat of vapourization

##### For Sublimation

Solid  $\rightleftharpoons$  Vapour

$$\Delta S_{sub} = S_{vapour} - S_{solid}$$

$$\Delta S_{sub} = \frac{\Delta H_{sub}}{T}$$

$\Delta H_{sub}$  = Heat of sublimation

#### 7. Entropy change when liquid is heated:

When a definite amount of liquid of mass ‘m’ and specific heat ‘s’ is heated

$$\partial q = m s T$$

$$\partial S = \frac{m s dT}{T}$$

$$\text{or } \Delta S = m s \log_e \frac{T_2}{T_1}$$

#### 8. Entropy Change in Mixing of Ideal Gases:

Suppose  $n_1$  mole of gas ‘P’ and  $n_2$  mole of gas ‘Q’ are mixed; then total entropy change can be calculate as:

$$\Delta S = -2.303 R [n_1 \log_{10} X_1 + n_2 \log_{10} X_2]$$

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Here  $X_1$  and  $X_2$  are mole fractions of gases P and Q respectively.

$$X_1 = \frac{n_1}{n_1 + n_2}.$$

$$X_2 = \frac{n_2}{n_1 + n_2}.$$

$$\Delta S/\text{mol} = -2.303R \left[ \frac{n_1 \log_{10} X_1}{n_1 + n_2} + \frac{n_2 \log_{10} X_2}{n_1 + n_2} \right]$$

$$\Delta S/\text{mol} = -2.303 R [X_1 \log_{10} X_1 + X_2 \log_{10} X_2]$$

### Some Facts About Entropy

- In nature all process are irreversible followed by an increase in entropy. Entropy of universe tends towards a maximum.

$$S_{\text{universe}} > 0$$

- $\Delta S_{\text{sys}} + \Delta S_{\text{surr.}} = 0$  for reversible process
- $S_{\text{sys}} + \Delta S_{\text{surr.}} > 0$  for irreversible process
- $\Delta S$  for a cyclic process and at the equilibrium state is zero.

- For a reversible process

$$S_{\text{total}} \text{ or } \Delta S_{\text{universe}} = 0$$

$$\text{So } \Delta S_{\text{system}} = \Delta S_{\text{surrounding}}$$

- For adiabatic reversible process entropy change is zero.

$$\Delta S_{\text{total}} = 0 \text{ so}$$

$$\text{Hence } \Delta S_{\text{system}} = \Delta S_{\text{surrounding}}$$

- Entropy change associated with change in temperature from  $T_2$  to  $T_1$  at constant pressure P is given as

$$\Delta S = 2.303 \times C_p \log \frac{T_2}{T_1}$$

- $C_p$  = Molar heat capacity at constant pressure.

### Some Examples of Entropy Change

- When a rubber band is stretched, entropy decreases because the macromolecules get uncoiled and hence arranged in a more ordered manner that is randomness decreases.
- When an egg is boiled, the entropy increases because denaturation occurs resulting into a change of proteins from helical form into random coiled form.

- Molecule kept in large volume container will have high entropy.
- Cases of increase in entropy—(1) dissolution of solute in water (2) decomposition of compound (3) vaporization and fusion (4) expansion of ideal gas from one container to an evacuated chamber.
- Decrease of entropy cases are crystallization, combination.
- Entropy is directly proportional to atomic weight for example—I<sub>2</sub> > Br<sub>2</sub> > Cl<sub>2</sub>
- Entropy is directly proportional to number of bonds example—Ethane > ethylene > ethene

### Physical Significance of Entropy

1. Randomness in a system  $\propto$  Entropy.
2. As according to the 2nd law of thermodynamics, the lost energy is directly proportional to absolute temperature during the process. Hence Entropy is unavailable energy of a system that is,  
Unavailable energy  $\propto$  Temperature  
Unavailable energy = Entropy  $\times$  temperature

$$\text{Entropy} = \frac{\text{Unavailable energy}}{\text{T in Kelvin}}$$

3. Entropy and Probability: It may be defined as a function of probability of a thermodynamic state as both entropy and thermodynamic probability increase simultaneously in a process so the state of equilibrium is the state of maximum probability.

Boltzman told that the entropy of a particular state is related to the number of ways that the state can be achieved as follows

$$S = K \ln W$$

Here W is the natural logarithm of the number of ways that the state can be achieved.

K is the Boltzman constant

$$K = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J/K.}$$

### Illustrations

29. Calculate the entropy change involved in the conversion of one mole of water at 373 K to vapour at the same temperature. (Latent heat of vapourization of water = 2.257 kJ g<sup>-1</sup>).

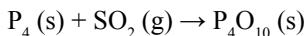
**Solution**  $\Delta S_v = \frac{\Delta H_v}{T_b}$

$$\Delta H_v = 2.257 \times 18 \times 10^3 \text{ J mol}^{-1}$$

$$T_b = 373 \text{ K}$$

$$\Delta S_v = \frac{2.257 \times 18 \times 10^3}{373} = 108.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

30. Calculate the standard entropy change associated with the following reaction at 298K.



$$\text{At } 298 \text{ K } S^\circ \text{ for } \text{P}_4 = 41.1 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$O_2 = 205.0 \text{ JK}^{-1} \text{ mol}^{-1} \text{ and}$$

$$P_4O_{10} = 231.0 \text{ JK}^{-1} \text{ mol}^{-1}$$

**Solution**  $\Delta S^\circ = \sum \Delta S^\circ_p - \sum \Delta S^\circ_r$

$$\Delta S^\circ = [\Delta S^\circ P_4O_{10} - (\Delta S^\circ P_4 + 5\Delta S^\circ O_2)]$$

$$= 231 - (41.1 + 5 \times 205.0)$$

$$= 231 - 1066.1 = -835.1 \text{ JK}^{-1} \text{ mol}^{-1}.$$

31. 5 moles of an ideal gas expand reversibly from a volume of 8 dm<sup>3</sup> to 80 dm<sup>3</sup> at a temperature of 27°C. Calculate the change in entropy.

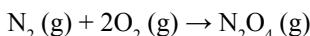
**Solution**  $\Delta S = 2.303 nR \log_{10} \frac{V_2}{V_1}$

$$\Delta S = 2.303 \times 5 \times 8.314 \times \log_{10} \frac{80}{8}$$

$$= 95.736 \times 1$$

$$= 95.736 \text{ JK}^{-1}$$

32. Calculate  $\Delta S_{sys}$ ,  $\Delta S_{surr}$ , and  $\Delta S_{total}$  at 25°C for the reaction



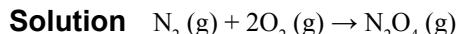
Is this reaction spontaneous under standard state conditions at 25°C?

Here  $\Delta H_f^\circ(\text{N}_2\text{O}_4) = 9.16 \text{ kJ}$ ,

$S^\circ(\text{N}_2) = 191.5 \text{ J K}^{-1} \text{ mol}^{-1}$ ,

$S^\circ(\text{O}_2) = 205.0 \text{ J K}^{-1} \text{ mol}^{-1}$ ,

$S^\circ(\text{N}_2\text{O}_4) = 304.2 \text{ J K}^{-1} \text{ mol}^{-1}$



$$\Delta H^\circ = \Delta H_f^\circ(\text{N}_2\text{O}_4) = 9.16 \text{ kJ}$$

$$\Delta S_{sys} = \Delta S^\circ = S^\circ(\text{N}_2\text{O}_4) - [S^\circ(\text{N}_2) + 2S^\circ(\text{O}_2)]$$

$$\Delta S_{sys} = (1)(304.2) - [(1)(191.5) - (2)(205.0)]$$

$$= -297.3 \text{ J/K}$$

$$\Delta S_{surr} = \frac{-\Delta H^\circ}{T} = -\frac{9.16 \text{ kJ}}{298} = -0.0307 \text{ kJ/K}$$

$$= -30.7 \text{ J/K}$$

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

$$= -297.3 \text{ J/K} + (-30.7 \text{ J/K})$$

$$= -328.0 \text{ J/K}$$

Because  $\Delta S_{total} < 0$ , the reaction is non-spontaneous.

33. Consider a two fold expansion of an ideal gas at 25°C in the isolated system.

(a) What are the values of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  for the process?

(b) How does this process illustrate the second law of thermodynamics?

**Solution** (a)  $\Delta H = 0$

$$\Delta S = R \ln \frac{V_{final}}{V_{initial}}$$

$$= (8.314 \text{ J/K}) \ln 2 = 5.76 \text{ J/K}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\text{As } \Delta H = 0, \Delta G = -T\Delta S$$

$$= -(298 \text{ K})(5.76 \text{ J/K})$$

$$= -1717 \text{ J} = -1.72 \text{ kJ}$$

(b) For a process in an isolated system,  $\Delta S_{surr} = 0$ . Therefore,  $\Delta S_{total} = \Delta S_{sys} > 0$ , and the process is spontaneous.

## Gibbs's Free Energy

It was introduced in order to relate  $H$ ,  $S$  and to explain spontaneity. According to J. Willard Gibbs's Free energy of a system is defined as the maximum

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amount of energy available to a system during a process that can be converted into useful work.

or

It is the thermodynamic quantity specially characterizing the system, the decrease in whose value during a process is equal to the useful work done by the system.

It is denoted by G and it is given mathematically as follows:

As enthalpy (H) is a function of S and P which is given as follows:

$$H = f(S, P)$$

$$dH = \left( \frac{\partial H}{\partial S} \right)_P dS + \left( \frac{\partial H}{\partial P} \right)_S dP \quad \dots \dots \text{(i)}$$

$$dH = TdS + VdP \quad \dots \dots \text{(ii)}$$

On comparing these two equation

$$\left( \frac{\partial H}{\partial S} \right)_P = T$$

On integrating equation (ii) we get,

$$\int dH = \int TdS + \text{Integration Constant}$$

$$= \int TdS + G$$

$$H = TS + G$$

$$G = H - TS$$

H = Enthalpy

T = Absolute temperature

S = Entropy

$$\text{As } H = E + PV$$

$$\text{So } G = E + PV - TS$$

Free energy change at constant temperature and pressure is given as:

$$\Delta G = \Delta E + P\Delta V - T\Delta S$$

$$\text{As } \Delta H = \Delta E + P\Delta V$$

$$\text{So } \Delta G = \Delta H - T\Delta S$$

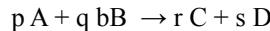
At standard conditions that is, 298 K and 1 atm pressure

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

It is called Gibbs Helmholtz's equation and it is used to explain criterion of spontaneity, driving force etc.

- It is a state function and an extensive property. So it is determined as  $\Delta G$  or  $\Delta G^\circ$ .

For a general reaction, it can be given as follows:



$$\Delta G^\circ = \sum \Delta G^\circ_p - \sum \Delta G^\circ_R$$

$$= [(r \sum \Delta G^\circ_C + s \sum \Delta G^\circ_D) - (p \cdot \sum \Delta G^\circ_A + q \sum \Delta G^\circ_B)]$$

### **ΔG and Criteria of Spontaneity**

Suppose we consider a system which is not isolated from its surroundings then for such a system  $\Delta S$  is given as:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \quad \dots \dots \text{(i)}$$

If we consider that  $q_p$  amount of heat is given by the system to the surroundings at constant temperature and constant pressure then

$$(q_p)_{\text{surroundings}} = -(q_p)_{\text{system}} = -\Delta H_{\text{system}}$$

$$\Delta S_{\text{surroundings}} = \frac{(q_p)_{\text{surroundings}}}{T} = \frac{-\Delta H_{\text{system}}}{T} \quad \dots \dots \text{(ii)}$$

So from equation (i) and (ii)

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T}$$

$$\text{or } T \Delta S_{\text{total}} = T \Delta S_{\text{system}} - \Delta H_{\text{system}}$$

$$-\Delta S_{\text{total}} = \Delta H_{\text{system}} - T \Delta S_{\text{system}} \quad \dots \dots \text{(iii)}$$

As according to Gibb-Helmholtz equation,

$$\Delta G = \Delta H - T\Delta S$$

$$\text{So } \Delta G_{\text{system}} = \Delta H_{\text{system}} - T \Delta S_{\text{system}}$$

$$\Delta G_{\text{system}} = -T \Delta S_{\text{total}}$$

As for spontaneous process

$$\Delta S_{\text{total}} > 0$$

$$\text{Hence } \Delta G = -ve$$

Thus for a spontaneous process  $T \Delta S_{\text{total}}$  must be positive or  $\Delta G$  must be negative.

**Case I:** Suppose both energy and entropy factors oppose a process that is,

$$\Delta H = +ve \text{ and } T \Delta S = -ve$$

$$\Delta G = \Delta H - T \Delta S$$

$$= (+ve) - (-ve) = +ve$$

Thus,  $\Delta G$  is positive for a non-spontaneous process.

**Case II:** Suppose both tendencies be equal in magnitude but opposite, that is,

$$\Delta H = +\text{ve} \text{ and } T\Delta S = +\text{ve}$$

$$\Delta H = T\Delta S$$

$$\Delta G = \Delta H - T\Delta S$$

$$= 0$$

Thus, the process is said to be at equilibrium.

**Case III:** Suppose entropy and energy, both factors are favourable for a process, that is,

$$\Delta H = -\text{ve} \text{ and } T\Delta S = +\text{ve}$$

$$\Delta G = \Delta H - T\Delta S$$

$$= (-\text{ve}) - (+\text{ve}) = -\text{ve}$$

Thus,  $\Delta G$  is negative for a spontaneous process.

$\Delta H$	$\Delta S$	$\Delta G = \Delta H - T\Delta S$	Remark
-	+	Always -ve	Spontaneous
+	-	Always +ve	Non-spon.
+	+	+ve at low temp -ve at high temp	Non spon. Spontaneous.
-	-	-ve at low temp +ve at high temp	Spontaneous Non-spon.

- $\Delta G = -\text{ve}$  (spontaneous process)
- $\Delta G = +\text{ve}$  (non spontaneous process)
- $\Delta G = 0$  (process in equilibrium)
- In exoergic reaction  $\Delta G = -\text{ve}$
- In endoergic reaction  $\Delta G = +\text{ve}$
- Temperature also plays an important role to decide the spontaneity of a process. A process which is not spontaneous at low temperature can become spontaneous at high temperature and vice-versa.

### Relationship between $\Delta G$ or $\Delta G^\circ$ with $E$ or $E^\circ$ :

Free energy change ( $\Delta G$ ) in an electrochemical cell can be related to electrical work done ( $E$ ) in cell as follows

$$\Delta G = -nFE$$

when we use standard conditions than

$$\Delta G^\circ = -nFE^\circ$$

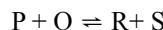
Here  $E^\circ$  = standard E.M.F of the cell

$n$  = No. of moles of  $e^-$  transferred

$F$  = Faraday's constant

### Relationship between $\Delta G^\circ$ and Equilibrium constant ( $K_{eq}$ )

for a reversible reaction



$\Delta G$ ,  $\Delta G^\circ$  and Reaction Quotient ( $Q$ ) are related as follows

$$\Delta G = \Delta G^\circ + RT \log_e Q$$

as at equilibrium  $\Delta G = 0$

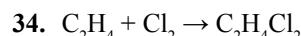
$$Q = K_{eq}$$

$$0 = \Delta G^\circ + RT \log_e K_{eq}$$

$$\Delta G^\circ = -RT \log_e K_{eq}$$

$$\Delta G^\circ = -2.303 RT \log_{10} K_{eq}$$

### Illustrations



$$\Delta H = -270.6 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

$$\Delta S = -139 \text{ J}$$

- Is the reaction favoured by entropy, enthalpy both or none?

- Find  $\Delta G$  it  $T = 300 \text{ K}$

### Solution

- As  $\Delta H =$  negative, exothermic process and is favoured, so it will be spontaneous.

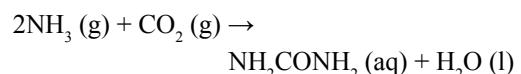
$$(ii) \Delta G = \Delta H - T\Delta S$$

$$= -270.6 \times 1000 - 300 \times (-139)$$

$$= -228900 \text{ J}$$

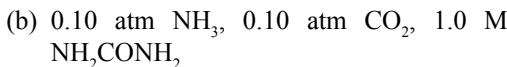
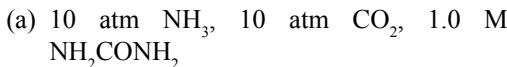
$$= -228.9 \text{ kJ}$$

- Urea ( $NH_2CONH_2$ ), an important nitrogen fertilizers is produced industrially by the reaction



Given that  $\Delta G^\circ = -13.6 \text{ kJ}$ , Calculate  $\Delta G$  at  $25^\circ\text{C}$  for the following set of conditions

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Is the reaction spontaneous for the conditions in part (a) or part (b)?

**Solution**  $\Delta G = \Delta G^\circ + RT \ln \frac{[\text{NH}_2\text{CONH}_2]}{(\text{PNH}_3)^2 (\text{PCO}_2)}$

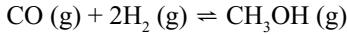
$$\begin{aligned} \text{(a)} \quad \Delta G &= -13.6 + [8.314 \times 10^{-3}] (298 \text{ K}) \ln [1.0/(10)^2 (10)] \\ &= -30.7 \text{ kJ/mol} \end{aligned}$$

As ΔG is negative, the reaction is spontaneous.

$$\begin{aligned} \text{(b)} \quad \Delta G &= -13.6 + [8.314 \times 10^{-3}] (298 \text{ K}) \ln [1.0/(0.10)^2 (0.10)] \\ &= +3.5 \text{ kJ/mol} \end{aligned}$$

As ΔG is positive, the reaction is non-spontaneous.

36. Calculate K<sub>p</sub> at 25°C for this reaction



What is ΔG for this reaction at 25°C when each reactant and product is present at a partial pressure of 20 atm?

$$\text{Here } \Delta G_f^\circ (\text{CH}_3\text{OH}) = -161.9 \text{ kJ/mol}$$

$$\Delta G_f^\circ (\text{CO}) = -137.2 \text{ kJ/mol}$$

**Solution**  $\text{CO (g)} + 2\text{H}_2 \text{ (g)} \rightleftharpoons \text{CH}_3\text{OH (g)}$

$$\Delta G^\circ = \Delta G_f^\circ (\text{CH}_3\text{OH}) - \Delta G_f^\circ (\text{CO})$$

$$\Delta G^\circ = 1 \times (-161.9) - (1) (-137.2) = -24.7 \text{ kJ}$$

$$\Delta G^\circ = -RT \ln K_p$$

$$\ln K_p = \frac{-\Delta G^\circ}{RT} = \frac{-(-24.7)}{(8.314 \times 10^{-3}) (298)} = 9.97$$

$$K_p = e^{9.97} = 2.1 \times 10^4$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$= (-24.7) + (8.314 \times 10^{-3}) + (298 \text{ K})$$

$$\ln \frac{[20]}{(20)(20)^2}$$

$$= -39.5 \text{ kJ/mol}$$

37. For a reaction  $\text{M}_2\text{O (s)} \rightarrow 2\text{M (s)} + \frac{1}{2}\text{O}_2 \text{ (g)}$ ;  $\Delta H = 30 \text{ kJ mol}^{-1}$  and  $\Delta S = 0.07 \text{ kJ K}^{-1} \text{ mol}^{-1}$  at atm. Calculate upto which temperature, the reaction would not be spontaneous.

### Solution

$$\Delta H = 30 \times 10^3 \text{ J mol}^{-1}$$

$$\Delta S = 70 \text{ JK}^{-1} \text{ mol}^{-1}$$

For a spontaneous reaction

$$\Delta G = +ve$$

$$\text{As } \Delta G = \Delta H - T\Delta S$$

So  $\Delta H - T\Delta S$  should be positive

$$\Delta H > T\Delta S$$

$$T < \frac{\Delta H}{\Delta S}$$

$$T < \frac{30 \times 10^3}{70}$$

$$T < 428.57 \text{ K}$$

## Enhance Your Knowledge

### Calorimeter

It is used to find enthalpy of reaction

$$\Delta H = \frac{Z \times \Delta T \times M}{W}$$

- It fails when (i) reaction is slow (ii) ΔH is low (iii) reaction does not complete
- ΔH does not change with temperature appreciably

### Resonance Energy

Resonance energy = Expected heat of hydrogenation – calculate heat of hydrogenation

Example,

Resonance energy of CO<sub>2</sub> is 32 calorie per mole.

- For adults, 2500–3000 Kcal energy per day is needed.

### Trauton's Law

$$\frac{\Delta H_{\text{vap}}}{T_b} = 88 \text{ Joule/K mol}$$

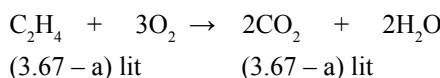
## Solved Problems from the IITs

1. A gas mixture of 3.67 litre of ethylene and methane on complete combustion at 25°C produces 6.11 litre of CO<sub>2</sub>. Calculate the heat evolved on burning 1 litre of the gas mixture. The heats of combustion of ethylene and methane are –1423 and –891 kJ mol<sup>–1</sup> at 25°C.

[IIT 1991]

**Solution** C<sub>2</sub>H<sub>4</sub> + 3O<sub>2</sub> → 2CO<sub>2</sub> + 2H<sub>2</sub>O

$$\text{a litre} \quad \quad \quad 2\text{a litre}$$



$$2\text{a} + 3.67 - \text{a} = 6.11$$

$$\text{a} = 2.44 \text{ litre}$$

Volume of ethylene in mixture = 2.44 litre

Volume of methane in mixture = 1.23 litre

$$\begin{aligned} \text{Volume of ethylene in 1 lit mixture} &= \frac{2.44}{3.67} \cdot \\ &= 0.6649 \text{ lit} \end{aligned}$$

$$\begin{aligned} \text{Volume of methane 1 lit mixture} &= \frac{1.23}{3.67} \cdot \\ &= 0.3351 \text{ lit} \end{aligned}$$

24.45 litre of a gas at 25°C correspond to 1 mole.

So heat evolved by burning 0.6649 litre of ethylene

$$= - \frac{1423}{24.5} \times 0.6649 = -38.69 \text{ kJ}$$

Heat evolved by burning 0.3351 litre of methane

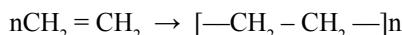
$$= - \frac{891}{24.45} \times 0.3351 = -12.21 \text{ kJ}$$

So total heat evolved by burning 1 litre of mixture

$$= -38.69 - 12.21$$

$$= -50.90 \text{ kJ}$$

2. The polymerization of ethylene to linear polyethylene is represented by the reaction



Where n has a large integral value. Given that the average enthalpies of bond dissociation for

C = C and C – C at 298 K are +590 and +331 kJ mol<sup>–1</sup> respectively, calculate the enthalpy of polymerization per mole of ethylene at 298 K.

[IIT 1995]

**Solution** During the polymerization of ethylene, one mole of ethylene breaks that is, one double bond breaks and the two CH<sub>2</sub>– groups are linked with single bonds so forming three single bonds. But in the whole unit of polymer, number of single bonds formed/mole of ethylene is 2.

Energy released = Energy due to formation of 2 single bonds

$$= 2 \times 331 = 662 \text{ kJ mol}^{-1} \text{ of ethylene}$$

Energy absorbed = Energy due to dissociation of 1 double bond

$$= 590 \text{ kJ mol}^{-1} \text{ of ethylene}$$

Enthalpy of polymerization/mol of ethylene or ΔH (Polymerization) = 590 – 662 kJ mol<sup>–1</sup>

$$= -72 \text{ kJ mol}^{-1}$$

3. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25°C are –156 and +49 kJ mol<sup>–1</sup> respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25°C is –119 kJ mol<sup>–1</sup>. Use these data of estimate to magnitude of the resonance energy of benzene.

[IIT 1996]

**Solution** Cyclohexene (l) + H<sub>2</sub> (g) → Cyclohexane (l)

$$\Delta H = -119 \text{ kJ}$$

Enthalpy of formation of cyclohexane (l)

$$= -156 \text{ kJ mol}^{-1}$$

So enthalpy of formation of cyclohexane

$$= -156 - (-119) \text{ kJ}$$

$$= -37 \text{ kJ mol}^{-1}$$

As ΔH<sub>Cyclohexane</sub> is –156 kJ mol<sup>–1</sup>, for every double bond the energy decreases by an amount +119 kJ mol<sup>–1</sup> and therefore for the introduction of three double bonds (present in benzene ring) the energy required.

## 4.30 ■ Energetics y

$$= 3 \times 119 \text{ kJ mol}^{-1} = 357 \text{ kJ mol}^{-1}$$

So, theoretical  $\Delta H_f$  for benzene

$$= (357 - 156) \text{ kJ mol}^{-1}$$

$$= 201 \text{ kJ mol}^{-1}$$

Resonance energy

$$= \text{Theoretical } \Delta H_f - \text{Observed } \Delta H_f$$

$$= (201 - 49) \text{ kJ mol}^{-1}$$

$$= 152 \text{ kJ mol}^{-1}$$

4. Compute the heat of formation of liquid methyl alcohol in kJ per mole using the following data. Heat of vapourization of liquid methyl alcohol = 38 kJ/mol. Heat of formation of gaseous atoms from the elements in their standard states are H = 218 kJ mol<sup>-1</sup>, C = 715 kJ mol<sup>-1</sup> and O = 249 kJ mol<sup>-1</sup>.

Average bond energies are:

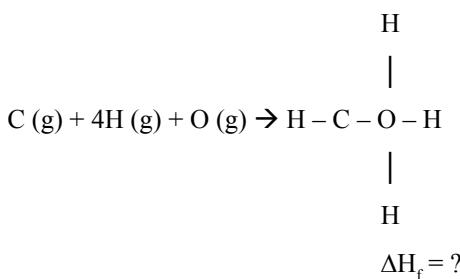
$$\text{C} - \text{H} = 415 \text{ kJ mol}^{-1}$$

$$\text{C} - \text{O} = 356 \text{ kJ mol}^{-1}$$

$$\text{O} - \text{H} = 463 \text{ kJ mol}^{-1}$$

[IIT 1997]

**Solution** The thermochemical reaction is as follows:



$$\begin{aligned} \Delta H_f &= [\Delta H_{\text{C}(\text{s}) \rightarrow \text{C}(\text{g})} + 2\Delta H_{\text{H}-\text{H}} + \frac{1}{2}\Delta H_{\text{O}} = 0] \\ &- [3\Delta H_{\text{C}-\text{H}} + \Delta H_{\text{C}-\text{O}} + \Delta H_{\text{O}-\text{H}} + \Delta H_{\text{vap. CH}_3\text{OH(l)}}] \\ &= [715 + 2 \times 436 + 249] - [3 \times 415 + 356 + 463 + 38] \\ &= 1836 - 2102 \text{ kJ mol}^{-1} \\ &= -266 \text{ kJ mol}^{-1} \end{aligned}$$

5. The enthalpy change involved in the oxidation of glucose is  $-2880 \text{ kJ mol}^{-1}$ . 25% of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer,

what is the maximum distance that a person will be able to walk after 120 g of glucose?

[IIT 1997]

**Solution** As energy available for muscular work by 1 mole of glucose

$$= \frac{2880 \times 25}{100} = 720 \text{ kJ mol}^{-1}$$

So 180 g glucose (mol. wt. of glucose) supplies 720 kJ.

$$120 \text{ g of glucose will supply} = \frac{720}{180} \times 120$$

$$= 480 \text{ kJ}$$

100 kJ is needed to walk 1 km.

$$480 \text{ kJ is needed to walk} \frac{1}{100} \times 480 = 4.8 \text{ km.}$$

6. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of CO<sub>2</sub>(g), H<sub>2</sub>O(l) and propene(g) are -393.5, -285.8 and 20.42 kJ mol<sup>-1</sup> respectively. The enthalpy of isomerization of cyclopropane to propene is -33.0 kJ mol<sup>-1</sup>.

[IIT 1998]

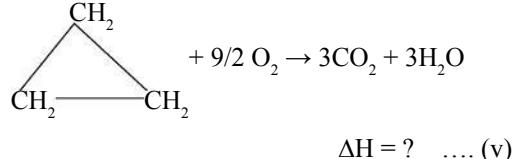
**Solution** C(s) + O<sub>2</sub>(g) → CO<sub>2</sub>(g);  $\Delta H = -393.5 \text{ kJ}$  ..... (i)

H<sub>2</sub>(g) + ½ O<sub>2</sub>(l) → H<sub>2</sub>O(l);  $\Delta H = -285.8 \text{ kJ}$  ..... (ii)

3C(s) + 3H<sub>2</sub>(g) → C<sub>3</sub>H<sub>6</sub>(g);  $\Delta H = 20.42 \text{ kJ}$  ..... (iii)

Cyclopropane → Propene(C<sub>3</sub>H<sub>6</sub>);  $\Delta H = -33.0 \text{ kJ}$  ..... (iv)

The required thermochemical reaction is



This equation (v) can be obtained by multiplying equation (i) and (ii) by 3, reversing equation (iii), keeping equation (iv) as such and adding, so formed new equation as follows:

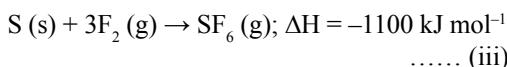
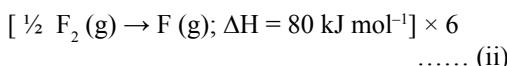
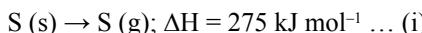
$$\Delta H = [(i) \times 3] + [(ii) \times 3] + [\text{Reverse of (iii)} + (\text{iv})]$$

$$\begin{aligned}
 &= [-393.5 \times 3] + [-285.8 \times 3] + [-20.42] + [-33.0] \\
 &= -1180.5 - 857.4 - 20.42 - 33.0 \\
 &= -2091.32 \text{ kJ.}
 \end{aligned}$$

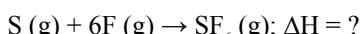
7. Estimate the average S – F bond energy in  $\text{SF}_6$ . The standard heat of formation values of  $\text{SF}_6$  (g), S (g) and F (g) are –1100, 275 and 80 kJ mol<sup>–1</sup> respectively.

[IIT 1999]

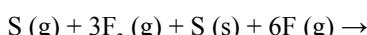
**Solution** Given



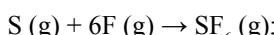
The required reaction



is obtained by adding the reverse of equations (i) and (ii) with the direct reaction (iii)



$$\Delta H = -1100 - 275 - 80 \times 6$$



$$\Delta H = -1855 \text{ kJ mol}^{-1}$$

Total bond energy in  $\text{SF}_6$  = 1855 kJ

Average S – F bond energy is  $\text{SF}_6$

$$= \frac{1855}{6} = 309.16 \text{ kJ mol}^{-1}$$

8. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm<sup>3</sup> to 2.50 dm<sup>3</sup>. Calculate the enthalpy change in this process.  $C_{v.m.}$  for argon is 12.48 J K<sup>–1</sup> mol<sup>–1</sup>.

[IIT 2000]

**Solution** Number of moles of argon present in the sample

$$= \frac{PV}{RT} = \frac{1.25 \times 1}{0.0821 \times 300} = 0.05075$$

For adiabatic expansion,

$$T_1/T_2 = (V_2/V_1)^{\gamma-1}$$

$$300/T_2 = (2.50/1.25)^{1.66-1}$$

$$T_2 = 188.55 \text{ K}$$

$$C_p = C_v + R$$

$$= 12.48 + 8.314$$

$$= 20.794 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H = n \times C_p \times \Delta T$$

$$= 0.05075 \times 20.794 \times (300 - 188.55)$$

$$= 117.6 \text{ J}$$

9. Show that the reaction,



at 300 K is spontaneous and exothermic, when the standard entropy change is –0.094 kJ mol<sup>–1</sup> K<sup>–1</sup>. The standard Gibbs free energies of formation for  $\text{CO}_2$  and CO are –394.4 and –137.2 kJ mol<sup>–1</sup> respectively.

[IIT 2000]

**Solution**  $\text{CO (g)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$

$$\Delta G^\circ = G^\circ(\text{CO}_2) - G^\circ(\text{CO}) - \frac{1}{2} G^\circ(\text{O}_2)$$

$$= -394.4 - (-137.2) - 0$$

$$= -257.2 \text{ kJ mol}^{-1}$$

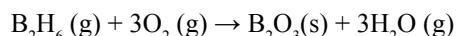
$$\Delta G^\circ = \Delta H^\circ - T\Delta S$$

$$-257.2 = \Delta H^\circ - 298 \times (0.094)$$

$$\Delta H^\circ = -288.2 \text{ kJ}$$

As  $\Delta G^\circ$  is negative so the process is spontaneous and  $\Delta H^\circ$  is also negative so the process is also exothermic.

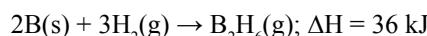
10. Diborane is a potential rocket fuel which undergoes combustion according to the reaction,



From the following data, calculate the enthalpy change for the combustion of diborane:



$$\Delta H = -1273 \text{ kJ}$$



[IIT 2000]

## 4.32 ■ Energetics



This reaction can be obtained as follows:

$$\text{Eq. (i)} + 3 \times \text{Eq. (ii)} + 3 \times \text{Eq. (iii)} - \text{Eq. (iv)}$$

$$= -1273 - 858 + 132 - 36$$

$$= -2035 \text{ kJ mol}^{-1}$$

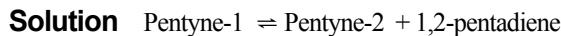
11. When 1-pentyne (A) is treated with 4N alcoholic KOH at  $175^\circ\text{C}$ , it is slowly converted into an equilibrium mixture of 1.3 % of 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1,2-pentadiene (C). The equilibrium was maintained at  $175^\circ\text{C}$ . Calculate  $\Delta G^\circ$  for the following equilibria:

$$\text{B} \rightleftharpoons \text{A} \quad \Delta G_1^\circ = ?$$

$$\text{B} \rightleftharpoons \text{C} \quad \Delta G_2^\circ = ?$$

From the calculated value of  $\Delta G_1^\circ$  and  $\Delta G_2^\circ$  indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C).

[IIT 2001]



(A)	(B)	(C)
$t_{\text{eq}}$ 1.3	95.2	3.5

$$K_{\text{eq}} = \frac{[\text{B}][\text{C}]}{[\text{A}]} = \frac{95.2 \times 3.5}{1.3} = 256.31$$

$$\text{B} \rightleftharpoons \text{A}$$

$$K_1 = \frac{[\text{A}]}{[\text{B}]} = \frac{[\text{C}]}{K_{\text{eq}}} = \frac{3.5}{256.31} = 0.013$$

$$\Delta G_1^\circ = -2.303 \text{ RT} \log_{10} K_1$$

$$= -2.303 \times 8.314 \times 448 \log_{10} 0.013$$

$$= 16178 \text{ J}$$

$$= 16.178 \text{ kJ}$$

$$\text{B} \rightleftharpoons \text{C}$$

$$K_2 = \frac{[\text{C}]}{[\text{B}]} = \frac{K_{\text{eq}} [\text{A}]}{[\text{B}]^2} = \frac{256.31 \times 1.3}{(95.2)^2} = 0.037$$

$$\Delta G_2^\circ = -2.303 \text{ RT} \log_{10} K_2$$

$$= -2.303 \times 8.314 \times 448 \log_{10} 0.037$$

$$= 12282 \text{ J} = 12.282 \text{ kJ}$$

The stability order is as follows:

$$\text{B} > \text{C} > \text{A}.$$

12. An insulated container contains 1 mole of a liquid, molar volume 100 ml at 1 bar. When liquid is steeply passed to 100 bar, volume decreases to 99 ml. Find the  $\Delta H$  and  $\Delta U$  for the process.

[IIT 2004]

**Solution** According to first law of thermodynamics

$$\Delta U = q + W$$

$$\Delta U = q + P\Delta V$$

$$= 0 + [-100 (99 - 100)]$$

$$= 100 \text{ bar ml}$$

$$\Delta H = \Delta U + (P_2 V_2 - P_1 V_1)$$

$$= 100 + (100 \times 99 - 1 \times 100)$$

$$= 9900 \text{ bar ml}$$

13. For the reaction,  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ ,  $\Delta H = -560 \text{ kJ}$ . Two moles of CO and one mole of  $\text{O}_2$  are taken in a container of volume 1 L. They completely form two moles of  $\text{CO}_2$ , the gases deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of  $\Delta U$  at 500 K.

$$(1 \text{ L atm} = 0.1 \text{ kJ})$$

[IIT 2006]

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = \Delta U + V\Delta P$$

$$\Delta U = \Delta H - V\Delta P = -560 + 1 \times 30 \times 0.1$$

$$= -557$$

$$\text{Absolute value} = 557 \text{ kJ}$$

## Calorimetry

Heat exchange

= Heat capacity  $\times$  temp change

(heat exchange – when no chemical change or state change occurs)

## MULTIPLE-CHOICE QUESTIONS

### Straight Objective Type Questions (Single Choice only)

1. Under the same conditions how many ml of 1 M KOH and 0.5 M  $\text{H}_2\text{SO}_4$  solutions, respectively, when mixed to form total volume of 100 ml, produces the highest rise in temperature?
  - a. 67, 33
  - b. 33, 67
  - c. 40, 60
  - d. 50, 50
2. Identify the state function among the following:
  - a. q
  - b.  $q - w$
  - c.  $q/w$
  - d.  $q + w$
3. For an endothermic reaction where  $\Delta H$  represents the enthalpy of the reaction in kJ/mol, the minimum value for the energy of activation will be
  - a. less than  $\Delta H$
  - b. zero
  - c. more than  $\Delta H$
  - d. equal to  $\Delta H$ .
4. Which of the following equations represent standard heat of formation of  $\text{C}_2\text{H}_4$ ?
  - a.  $2\text{C}(\text{diamond}) + 2\text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g})$
  - b.  $2\text{C}(\text{graphite}) + 2\text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g})$
  - c.  $2\text{C}(\text{diamond}) + 4\text{H}(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g})$
  - d.  $2\text{C}(\text{graphite}) + 4\text{H}(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g})$
5. A glucose solution in 100 gm of water boils at  $100.26^\circ\text{C}$ . If this solution is heated to  $101^\circ\text{C}$ . What will be the mass of water left at equilibrium?
  - a. 76 gm
  - b. 120 gm
  - c. 100 gm
  - d. 26 gm
6. The enthalpy of hydrogenation of cyclohexene is  $-119.5 \text{ kJ mol}^{-1}$ . If resonance energy of benzene is  $-150.4 \text{ kJ mol}^{-1}$ , its enthalpy of hydrogenation would be
  - a.  $-269.9 \text{ kJ mol}^{-1}$
  - b.  $-358.5 \text{ kJ mol}^{-1}$
  - c.  $-508.9 \text{ kJ mol}^{-1}$
  - d.  $-208.1 \text{ kJ mol}^{-1}$
7. A reaction is non-spontaneous at the freezing point of water but is spontaneous at the boiling point of water then

$\Delta$	$\Delta$
a. +ve	+ve
b. -ve	-ve
c. -ve	+ve
d. +ve	-ve

8. The enthalpy change ( $\Delta H$ ) for the reaction,  
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$   
 is  $-92.38 \text{ kJ}$  at  $298 \text{ K}$ . The internal energy change  $\Delta U$  at  $298 \text{ K}$  is
 

a. $-92.38 \text{ kJ}$	b. $-87.42 \text{ kJ}$
c. $-97.34 \text{ kJ}$	d. $-89.9 \text{ kJ}$
9. For a phase change
 
$$\text{H}_2\text{O}(\text{l}) \xrightleftharpoons[0^\circ\text{C}, 1 \text{ bar}]{\hspace{1cm}} \text{H}_2\text{O}(\text{s})$$

a. $\Delta G = 0$	b. $\Delta S = 0$
c. $\Delta H = 0$	d. $\Delta U = 0$
10. The enthalpy and entropy change for the reaction  
 $\text{Br}_2(\text{l}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{BrCl}(\text{g})$   
 are  $30 \text{ kJ mol}^{-1}$  and  $105 \text{ J K}^{-1} \text{ mol}^{-1}$  respectively. The temperature at which the reaction will be in equilibrium is
 

a. 450 K	b. 300 K
c. 285.7 K	d. 273 K
11. For a spontaneous process, the correct statement is
  - a. entropy of the system always increases
  - b. free energy of the system always increases
  - c. total entropy change is always negative
  - d. total entropy change is always positive
12. A heat engine absorbs heat  $q_1$  from a source at temperature  $T_1$  and heat  $q_2$  from a source at temperature  $T_2$ . Work done is found to be  $J(q_1 + q_2)$ . This is in accordance with:
  - a. first law of thermodynamics
  - b. second law of thermodynamics
  - c. joules equivalent law
  - d. none of these
13. Identify the correct statement for change of Gibb's energy for a system ( $\Delta G_{\text{system}}$ ) at constant temperature and pressure:
  - a. if  $\Delta G_{\text{system}} = 0$ , the system is still moving in a particular direction

## 4.34 ■ Energetics

- b.** if  $\Delta G_{\text{system}} = -\text{ve}$ , the process is not spontaneous  
**c.** if  $\Delta G_{\text{system}} = +\text{ve}$ , the process is spontaneous  
**d.** if  $\Delta G_{\text{system}} = 0$ , the system has attained equilibrium
- 14.** For the reaction of one mole of Zn –dust with one mole of  $\text{H}_2\text{SO}_4$  in a bomb calorimeter,  $\Delta U$  an W corresponds to:
- $\Delta U < 0, W = 0$
  - $\Delta U < 0, W < 0$
  - $\Delta U > 0, W = 0$
  - $\Delta U > 0, W > 0$
- 15.**  $\Delta H_f^\circ$  (298) of methanol is given by chemical equation
- $\text{CH}_4(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{g})$
  - $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{l})$
  - $\text{C}(\text{graphite}) + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{l})$
  - $\text{C}(\text{diamond}) + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{l})$
- 16.** Assume each reaction is carried out in an open container. For which reaction will  $\Delta H = \Delta U$ ?
- $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
  - $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$
  - $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$
  - $\text{C}(\text{s}) + 2\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}_2(\text{g}) + \text{CO}_2(\text{g})$
- 17.** The absolute enthalpy of neutralization of the reaction
- $$\text{MgO}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$$
- will be
- 57.33 kJ/mole
  - >-57.33 kJ/ mole
  - <-57.33 kJ/mole
  - 57.33 kJ /mole.
- 18.** A reaction occurs spontaneously if
- $T\Delta S < \Delta H$  and both  $\Delta H, \Delta S$  are +ve
  - $T\Delta S > \Delta H$  and  $\Delta H = +\text{ve}, \Delta S = -\text{ve}$
  - $T\Delta S > \Delta H$  and both  $\Delta H, \Delta S$  are +ve
  - $T\Delta S = \Delta H$  and both  $\Delta H, \Delta S$  are +ve
- 19.** If at 298 K the bond energies of C–H, C–C, C=C and H–H bonds are respectively 414, 347, 615 and 435 kJ mol<sup>-1</sup>, the value of enthalpy change for the reaction
- $$\text{H}_2\text{C}=\text{CH}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{H}_3\text{C}-\text{CH}_3(\text{g})$$
- at 298 K will be
- a.** +250 kJ                   **b.** -250 kJ  
**c.** +125 kJ                   **d.** -125 kJ
- 20.** A gas expands into a vacuum (external pressure = 0) while in thermal isolation from the surroundings. For this expansion
- $\Delta E$  does not change
  - $\Delta E$  increases
  - $\Delta E = T^{\circ}\text{S}$
  - $\Delta E$  decreases
- 21.** For a process at constant volume,
- $w = 0$  and  $\Delta E = \Delta H$
  - $w = 0$  and  $\Delta H = q$
  - $q = 0, w = 0$  and  $\Delta E = 0$
  - $w = 0$  and  $\Delta E = q$
- 22.** In an irreversible process taking place at constant T and P and in which only pressure –volume work is being done, the change in Gibbs free energy ( $dG$ ) and change in entropy ( $dS$ ), satisfy the criteria:
- $(dS)_{V,E} < 0, (dG)_{T,P} < 0$
  - $(dS)_{V,E} > 0, (dG)_{T,P} < 0$
  - $(dS)_{V,E} = 0, (dG)_{T,P} = 0$
  - $(dS)_{V,E} = 0, (dG)_{T,P} > 0$
- 23.** Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction?
- exothermic and increasing disorder
  - exothermic and decreasing disorder
  - endothermic and increasing disorder
  - endothermic and decreasing disorder
- 24.** The internal energy change when a system goes from state A to B is 40 kJ/mol. if the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy?
- 40 kJ
  - > 40 kJ
  - < 40 kJ
  - zero
- 25.** Standard state Gibbs free energy change for isomerization reaction,
- $$\text{Cis-2-pentene} \leftrightarrow \text{trans-2-pentene}$$
- is -3.67 kJ/mol at 400 K. if more trans-2-pentene is added to the reaction vessel, then:
- more cis-2-pentene is formed
  - additional trans-2-pentene is formed
  - equilibrium remains unaffected
  - equilibrium is shifted in the forward direction

- 26.** An ideal gas expands in volume from  $1 \times 10^{-3} \text{ m}^3$  to  $1 \times 10^{-2} \text{ m}^3$  at 300 K against a constant pressure of  $1 \times 10^5 \text{ Nm}^{-2}$ . The work done is
- 900 kJ
  - 900 J
  - 270 kJ
  - 940 kJ
- 27.** For a reaction to occur spontaneously
- $(\Delta H - T\Delta S)$  must be negative
  - $(\Delta H + T\Delta S)$  must be negative
  - $\Delta H$  must be negative
  - $\Delta S$  must be negative
- 28.** Which one of the following has  $\Delta S^\circ$  greater than zero?
- $\text{CaO (s)} + \text{CO}_2(\text{g}) \leftrightarrow \text{CaCO}_3(\text{g})$
  - $\text{NaCl (aq)} \leftrightarrow \text{NaCl (s)}$
  - $\text{NaNO}_3(\text{s}) \leftrightarrow \text{Na}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$
  - $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \leftrightarrow 2\text{NH}_3(\text{g})$
- 29.** For an explosion in an open vessel, one would expect
- $\Delta H$  to be negative and  $\Delta E$  to be greater than  $\Delta H$
  - $\Delta H$  to be negative and  $\Delta E$  to be less than  $\Delta H$
  - $\Delta H$  to be positive and  $\Delta E$  to be less than  $\Delta H$
  - $\Delta H$  to be positive and  $\Delta E$  to be greater than  $\Delta H$
- 30.** Which of the following is correct equation?
- $\Delta U = \Delta Q - W$
  - $\Delta W = \Delta U + \Delta Q$
  - $\Delta U = \Delta W + \Delta Q$
  - none of these
- 31.** Consider the reaction  $\text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3$  carried out at constant temperature and pressure. If  $\Delta H$  and  $\Delta U$  are the enthalpy and internal energy changes for the reaction. Which of the following expressions is true?
- $\Delta H = 0$
  - $\Delta H = \Delta U$
  - $\Delta H < \Delta U$
  - $\Delta H > \Delta U$
- 32.** 1 mol of an ideal gas at 300 K is expanded isothermally and reversible from an initial volume of 1 litre to 10 litre. The work in this process is ( $R = 2 \text{ cal mol}^{-1} \text{ K}^{-1}$ )
- 163.7 cal
  - zero
  - 1381.8 cal
  - 9 litre atm
- 33.** Identify the correct statement regarding entropy.
- At absolute zero temperature, entropy of a perfectly crystalline substance is taken to be zero
  - At absolute zero of temperature the entropy of a perfectly crystalline substance is +ve
  - At absolute zero of temperature the entropy of all crystalline substance is to be zero
- 34.** A gas expands against a non-zero external pressure while in thermal isolation from the surroundings. For this expansion
- $\Delta E = q$
  - $\Delta E$  increases
  - $\Delta E$  does not change
  - $\Delta E$  decreases
- 35.** The standard enthalpy of formation ( $\Delta H^\circ$ ) at 298 K for methane,  $\text{CH}_4(\text{g})$  is  $-74.8 \text{ kJ mol}^{-1}$ . the additional information required to determine the average energy for C – H bond formation would be
- the dissociation energy of  $\text{H}_2$  and enthalpy of sublimation of carbon
  - latent heat of vapourization of methane
  - the first four ionization energies of carbon and electron gain enthalpy of hydrogen
  - the dissociation energy of hydrogen molecule,  $\text{H}_2$
- 36.** The factor of  $\Delta G$  values is important in metallurgy. The  $\Delta G$  values for the following reactions at 800°C are given as
- $$\text{S}_2(\text{s}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{SO}_2(\text{g}) ; \Delta G = -544 \text{ kJ}$$
- $$2\text{Zn}(\text{s}) + \text{S}_2(\text{s}) \rightarrow 2\text{ZnS}(\text{s}) ; \Delta G = -293 \text{ kJ}$$
- $$2\text{Zn}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{ZnO}(\text{s}) ; \Delta G = -480 \text{ kJ}$$
- the  $\Delta G$  for the reaction,
- $$2\text{ZnS}(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{ZnO}(\text{s}) + 2\text{SO}_2(\text{g})$$
- will be
- 357 kJ
  - 731 kJ
  - 773 kJ
  - 229 kJ
- 37.** An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If  $T_i$  is the initial temperature and  $T_f$  is the final temperature, which of the following statements is correct?
- $(T_f)_{\text{irrev}} > (T_p)_{\text{rev}}$
  - $T_f > T_i$  for reversible process but  $T_f = T_i$  for irreversible process
  - $(T_p)_{\text{irrev}} = (T_p)_{\text{rev}}$
  - $T_f = T_i$  for both reversible and irreversible processes
- 38.** The entropy change in the fusion of 1 mol of a solid melting at 27°C (Latent heat of fusion,  $2930 \text{ J mol}^{-1}$ ) is
- $9.77 \text{ JK}^{-1} \text{ mol}^{-1}$
  - $10.73 \text{ JK}^{-1} \text{ mol}^{-1}$

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- c.  $2930 \text{ JK}^{-1} \text{ mol}^{-1}$   
d.  $108.5 \text{ JK}^{-1} \text{ mol}^{-1}$
39. As a given temperature and pressure, which of the following would be expected to have the greatest molar entropy?  
a.  $\text{Br}_2(\text{g})$   
b.  $\text{Br}_2(\text{s})$   
c.  $\text{Br}_2(\text{l})$   
d. All of these would be expected to have the same molar entropy.
40. The standard enthalpy of formation ( $\Delta_f H^\circ$ ) at 298 K for methane,  $\text{CH}_4(\text{g})$  is  $-74.8 \text{ kJ mol}^{-1}$ . the additional information required to determine the average energy for C – H bond formation would be  
a. the dissociation energy of  $\text{H}_2$  and enthalpy of sublimation of carbon  
b. latent heat of vapourization of methane  
c. the first four ionization energies of carbon and electron gain enthalpy of hydrogen  
d. the dissociation energy of hydrogen molecule,  $\text{H}_2$
41. When 1 mol gas is heated at constant volume temperature is raised from 298 to 308 K. Heat supplied to the gas is 500 J. Then which statement is correct?  
a.  $q = W = 500 \text{ J}$ ,  $\Delta U = 0$   
b.  $q = \Delta U = 500 \text{ J}$ ,  $W = 0$   
c.  $q = W = 500 \text{ J}$ ,  $\Delta U = 0$   
d.  $\Delta U = 0$ ,  $q =$
42. For the reaction:  
 $\text{S}_8(\text{s}) + 8\text{O}_2(\text{g}) \rightarrow 8\text{SO}_2(\text{g})$   
a.  $\Delta H < \Delta E$   
b.  $\Delta H = \Delta E$   
c.  $\Delta H > \Delta E$   
d.  $\Delta H$  is independent of the physical state of reactants.
43. 2 mol of an ideal gas at  $27^\circ\text{C}$  temperature is expanded reversibly from 2 L to 20 L. Find entropy change in cal. ( $R = 2 \text{ cal/mol K}$ )  
a. 92.1  
b. 0  
c. 4  
d. 9.2
44.  $(\Delta H - \Delta U)$  for the formation of carbon monoxide (CO) from its elements at 298 K is  
a.  $-1238.78 \text{ J mol}^{-1}$   
b.  $1238.78 \text{ J mol}^{-1}$
- c.  $-2477.57 \text{ J mol}^{-1}$   
d.  $2477.57 \text{ J mol}^{-1}$
45. For the reaction,  
 $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$  at constant temperature,  $\Delta H - \Delta E$  is  
a.  $+3\text{RT}$   
b.  $-\text{RT}$   
c.  $+\text{RT}$   
d.  $-3\text{RT}$
46. What is the entropy change (in  $\text{JK}^{-1} \text{ mol}^{-1}$ ) when 1 mol of ice is converted into water at  $0^\circ\text{C}$ ? (The enthalpy change for the conversion of ice to liquid water is  $6.0 \text{ kJ mol}^{-1}$  at  $0^\circ\text{C}$ )  
a. 2.198  
b. 21.98  
c. 20.13  
d. 2.013
47. An ideal gas expand against a constant external pressure of 5.0 atmosphere from 40 to 60 litre and absorb 40 kJ of energy from surrounding. The change in internal energy of the system will be  
a. 20.52 kJ  
b. 52.75 kJ  
c. 32.75 kJ  
d. 35.95 kJ
48. The molar heat capacity of water at constant pressure,  $C$ , is  $75 \text{ JK}^{-1} \text{ mol}^{-1}$ . When 1.0 kJ of heat is supplied to 100 g of water which is free to expand, the increase in temperature of water is  
a. 4.8 K  
b. 6.6 K  
c. 1.2 K  
d. 2.4 K
49. The incorrect statement amongst the following is  
a. at equilibrium  $\Delta H_{\text{S}, \text{P}} = 0$   
b. the condition of equilibrium at constant P and T is that G must be minimum  
c. at equilibrium  $\Delta G_{\text{P}, \text{T}} = 0$   
d.  $\Delta G^\circ$  calculated using the equation;  $\Delta G^\circ = -RT \ln K_p$ , is the free energy change of the reaction when each of the species (reactants and products) is in the standard state of unit activity that is, roughly unit concentration.
50. The heat liberated on complete combustion of 7.8 gm of benzene is 327 kJ. This heat was measured at constant volume and at  $27^\circ\text{C}$ . Calculate the heat of combustion of benzene at constant pressure ( $R = 8.3 \text{ J/mole/K}$ )  
a.  $-1637 \text{ kJ/mole}$   
b.  $-3274 \text{ kJ/mole}$   
c.  $-3270 \text{ kJ/mole}$   
d. none of these
51. AB,  $\text{A}_2$  and  $\text{B}_2$  are diatomic molecule if the bond enthalpies of  $\text{A}_2$ , AB and  $\text{B}_2$  are in the ratio  $1:1:0.5$  and the enthalpy of formation of AB from A and  $\text{B}_2$  is  $100 \text{ kJ/mole}$ . What is the bond enthalpy of  $\text{A}_2$ ?

- 52.** Considering entropy ( $S$ ) as a thermodynamic parameter, the criterion for the spontaneity of any process is
- 400 kJ/mole
  - 300 kJ/mole
  - 200 kJ/mole
  - 100 kJ/mole
- 53.** The gas in a refrigerator causes cooling on expansion because
- work done by the gas is converted into heat
  - heat of the gas is lost as work is done by the gas
  - the heat is spread over a larger space
  - None
- 54.** The standard heats of formation of  $\text{NO}_2$  (g) and  $\text{N}_2\text{O}_4$  (g) are 8.0 and 2.0 kcal  $\text{mol}^{-1}$  respectively. The heat of dimerization of  $\text{NO}_2$  in kcal is
- 10.0
  - 6.0
  - 12.0
  - 14.0
- 55.** Calculate the work done during isothermal expansion of one mole of an ideal gas from 10 atm to 1 atm at 300K.
- 1382 cal
  - 1382 joule
  - 13.82 cal
  - 1.382 cal
- 56.** The heats of neutralization of four acids a, b, c and d when neutralized against a common base and 13.7, 9.4, 11.2 and 12.4 kcal respectively. the weakest among these acids is
- a
  - b
  - c
  - d
- 57.** Which of the following salts shall cause maximum cooling when one mole of the salt is dissolved in the same amount of water? (integral heat of solution at 298 K is given for each solute)
- $\text{KNO}_3$ ,  $\Delta H = 35.4 \text{ kJ mol}^{-1}$
  - $\text{NaCl}$ ,  $\Delta H = -5.35 \text{ kJ mol}^{-1}$
  - $\text{KOH}$ ,  $\Delta H = -55.6 \text{ kJ mol}^{-1}$
  - $\text{KBr}$ ,  $\Delta H = -83.3 \text{ kJ mol}^{-1}$
- 58.** The melting point of a solid is  $27^\circ\text{C}$  and it's latent heat of fusion is 600 calories per mole. The entropy change for the fusion of one mole of the solid (in  $\text{cal K}^{-1}$ ) is
- 180
  - 22.2
  - 2
  - 0.5
- 59.** Devitrification of glass is a process for which change in entropy ( $\Delta S$ )
- 60.** In a flask, colourless  $\text{N}_2\text{O}_4$  is in equilibrium with brown coloured  $\text{NO}_2$ . At equilibrium, the brown colour deepens on heating the flask to  $100^\circ\text{C}$  and on cooling it become less coloured.  $\Delta H$  for the system is
- positive
  - negative
  - zero
  - undefined
- 61.** Which of the following modes of energy constitute both kinetic and potential energy?
- nuclear energy
  - transitional energy
  - rotational energy
  - vibrational energy
- 62.** Which of the following is not expected to be correct?
- $\Delta H_f^\circ (\text{CO}_2) = \text{negative}$
  - $\Delta H_{\text{comb}} (\text{NO}) = \text{positive}$
  - $\Delta H_{\text{hyd}} (\text{BaCl}_2) = \text{negative}$
  - $\Delta H_{\text{neut}} = \text{negative}$
- 63.** The standard heat of formation of diamond is
- same as that of graphite
  - greater than that of graphite
  - less than that of graphite
  - taken as zero
- 64.** How many calories are required to heat 40 gram of argon from 40 to  $100^\circ\text{C}$  at constant volume? ( $R = 2 \text{ cal/mol.K}$ )
- 120
  - 180
  - 1800
  - 2400
- 65.** Which of the following does not express criterion of spontaneity?
- $(dS)_{\text{P.T.}} > 0$
  - $(dA)_{\text{V.T.}} \geq 0$
  - $(dG)_{\text{P.T.}} < 0$
  - All of these
- 66.** Which one of the following set of units represents the smallest and the largest amount of energy respectively?
- eV and lit atm
  - Cal and eV
  - J and erg
  - erg and cal

## 4.38 ■ Energetics

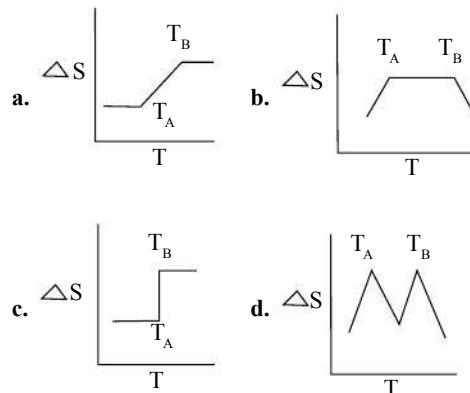
67. If  $K < 1.0$ , what will be the value of  $\Delta G^\circ$  of the following?
- Zero
  - Negative
  - Positive
  - 1.0
68. Which of the following are not state functions?
- $q + w$
  - $q$
  - $w$
  - $H - TS$
- (I), (II) and (III)
  - (II) and (III)
  - (I) and (IV)
  - (II), (III) and (IV)
69. Oxidizing power of chlorine in aqueous solution can be determined by the parameters indicated below:
- $$\frac{1}{2} \text{Cl}_2(\text{g}) \xrightarrow{\frac{1}{2} \Delta_{\text{diss}} \text{H}^-} \text{Cl}(\text{g}) \xrightarrow{\Delta_{\text{eg}} \text{H}^-}$$
- $$\text{Cl}^-(\text{g}) \xrightarrow{\Delta_{\text{hyd.}} \text{H}^-} \text{Cl}^-(\text{aq})$$
- The energy involved in the conversion of  $\frac{1}{2} \text{Cl}_2(\text{g})$  to  $\text{Cl}^-(\text{g})$  (Using the data,  $\Delta_{\text{diss}} \text{H}^- \text{Cl}_2 = 240 \text{ kJ mol}^{-1}$ ,  $\Delta_{\text{eg}} \text{H}^- \text{Cl} = -349 \text{ kJ mol}^{-1}$ ,  $\Delta_{\text{hyd.}} \text{H}^- \text{Cl} = -381 \text{ kJ mol}^{-1}$ ) will be
- $+152 \text{ kJ mol}^{-1}$
  - $-610 \text{ kJ mol}^{-1}$
  - $-850 \text{ kJ mol}^{-1}$
  - $+120 \text{ kJ mol}^{-1}$
70. For the gas phase reaction,
- $$\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$$
- Which of the following conditions are correct?
- $\Delta H < 0$  and  $\Delta S < 0$
  - $\Delta H > 0$  and  $\Delta S < 0$
  - $\Delta H = 0$  and  $\Delta S < 0$
  - $\Delta H > 0$  and  $\Delta S > 0$
71. Using the following thermochemical equations
- $\text{S}_{(\text{th})} + 3/2 \text{O}_{2(\text{g})} \rightarrow \text{SO}_{3(\text{g})}; \Delta H = -2x \text{ kJ mol}^{-1}$
  - $\text{SO}_{2(\text{g})} + 1/2 \text{O}_{2(\text{g})} \rightarrow \text{SO}_{3(\text{g})}; \Delta H = -y \text{ kJ mol}^{-1}$
- Find out the heat of formation of  $\text{SO}_{2(\text{g})}$  in  $\text{kJ mol}^{-1}$ .
- $(x + y)$
  - $(2x + y)$
  - $(2x/y)$
  - $(y - 2x)$
  - $(2x - y)$
72. When compared to  $\Delta G^\circ$  for the formation of  $\text{Al}_2\text{O}_3$ , the  $\Delta G^\circ$  for the formation of  $\text{Cr}_2\text{O}_3$  is
- Lower
  - Unpredicted
  - Higher
  - Same
73. For one mole of ammonia and one mole of hydrogen chloride are mixed in a closed container to form ammonium chloride gas, then
- $\Delta H = \Delta U$
  - $\Delta H < \Delta U$
  - There is no relationship
  - $\Delta H > \Delta U$
74. At a given pressure and volume, in the  $P - V$  plot, of an ideal gas,
- $$\frac{\text{Slope of an adiabatic curve}}{\text{Slope of an isothermal curve}}$$
- is
- $C_p/R$
  - $C_v/C_p$
  - $C_p C_v$
  - $R$
75. Enthalpy is equal to
- $-T^2 [\partial(G/T)/\partial T]_V$
  - $T^2 [\partial(G/T)/\partial T]_V$
  - $-T^2 [\partial(G/T)/\partial T]_P$
  - $T^2 [\partial(G/T)/\partial T]_P$

### Brainteasers Objective Type Questions (Single choice only)

76. The standard molar enthalpies of formation of cyclohexane ( $\text{l}$ ) and benzene ( $\text{l}$ ) at  $25^\circ\text{C}$  are— $156$  and  $+49 \text{ kJ mol}^{-1}$  respectively. The standard enthalpy of hydrogenation of Cyclohexene ( $\text{l}$ ) at  $25^\circ\text{C}$  is  $-119 \text{ kJ/mol}$ . Find resonance energy of benzene.
- $-152 \text{ kJ mol}^{-1}$
  - $-159 \text{ kJ mol}^{-1}$
  - $+152 \text{ kJ mol}^{-1}$
  - $+159 \text{ kJ mol}^{-1}$
77. 0.50mol of ammonium nitrate is added to 50.0 mL or water in a thermally insulated reaction vessel. Both are initially at  $20.0^\circ\text{C}$ . After stirring the temperature of the solution is found to be less than  $10^\circ\text{C}$ . Which statement best explains the temperature change?
- Heat is evolved from the system to the surroundings.
  - Heat is absorbed from the surroundings by the system.
  - Heat is absorbed by ammonium nitrate when it dissolves and becomes hydrated.

- d. Heat is evolved by ammonium nitrate when it dissolves and becomes hydrated.
- e. The heat energy of the hydrated ions is less than the ions in solid ammonium nitrate.
78. Determine the sign of  $\Delta S^\circ$  for each of the following processes:
- (I)  $C_6H_6(s) \rightarrow C_6H_6(l)$
- (II)  $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
- a.  $\Delta S^\circ$  should be positive for I and positive for II.  
b.  $\Delta S^\circ$  should be positive for I and negative for II.  
c.  $\Delta S^\circ$  should be negative for I and negative for II.  
d.  $\Delta S^\circ$  should be negative for I and positive for II.
79. The difference between heats of reaction at constant pressure and constant volume for the reaction  
 $2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$   
at  $25^\circ C$  in kJ is
- a. -7.43      b. +3.72  
c. -3.72      d. + 7.43
80. 100 ml of 0.3 M HCl solution is mixed with 100 ml of 0.33 M KOH solution. The amount of heat liberated is
- a. 1.713 kJ      b. 17.42 kJ  
c. 1.31 kJ      d. 17.13 kJ
81. An athlete is given 100 g of glucose of energy equivalent to 1560 kJ. He utilizes 50 % of this gained energy in the event. In order to avoid storage of energy in the body, calculate the mass of water he would need to perspire. Enthalpy of  $H_2O$  for evaporation is  $44\text{ kJ mol}^{-1}$ .
- a. 346 g      b. 316 g  
c. 323 g      d. 319 g
82. The enthalpies of formation of  $CO_2(g)$  and  $CO(g)$  at  $298\text{ K}$  are in the ratio 2.56: 1. For the reaction,  
 $CO_2(g) + C(s) \rightarrow CO(g)$ ,  $\Delta H = 177.5\text{ kJ}$ ,  $\Delta H_f$  of  $CO(g)$  is
- a.  $-113.78\text{ kJ mol}^{-1}$   
b.  $113.78\text{ kJ mol}^{-1}$   
c.  $-141.6\text{ kJ mol}^{-1}$   
d.  $-180.6\text{ kJ mol}^{-1}$
83. If for a given substance,  $T_B$  is the m.p. and  $T_A$  is the freezing point, then correct variation of entropy

by graph between entropy change ( $\Delta S$ ) and temperature is

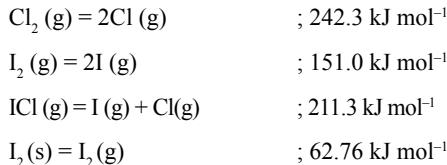


84. The standard enthalpy of combustion at  $25^\circ C$  of  $H_2$ ,  $C_6H_{10}$  and cyclohexane ( $C_6H_{12}$ ) are  $-241$ ,  $-3800$  and  $-3920\text{ kJ mol}^{-1}$  respectively. Calculate heat of hydrogenation of cyclohexane ( $C_6H_{10}$ )
- a.  $-161\text{ kJ mol}^{-1}$       b.  $-131\text{ kJ mol}^{-1}$   
c.  $-121\text{ kJ mol}^{-1}$       d. None
85. Classify each of the following processes as spontaneous or non spontaneous.
- I.  $H_2O(l) \rightarrow H_2O(g)$   $T = 25^\circ C$  vessel open to atmosphere with 50 % relative humidity.
- II.  $H_2O(s) \rightarrow H_2O(l)$   $T = 25^\circ C$ ,  $P = 1\text{ atm}$
- a. I and II are both non spontaneous  
b. I and II are both spontaneous  
c. I is non spontaneous and II is spontaneous  
d. I is spontaneous and II is non spontaneous.
86. The standard heats of formation of  $CH_4(g)$ ,  $CO_2(g)$  and  $H_2O(g)$  are  $-76.2$ ,  $-394.8$  and  $-241.6\text{ kJ mol}^{-1}$  respectively. Calculate the amount of heat evolved by burning  $1m^3$  methane measured under normal conditions.
- a.  $162897.3\text{ kJ}$       b.  $64078.2\text{ kJ}$   
c.  $35182\text{ kJ}$       d. none
87. For an explosion in an open vessel, one would expect
- a.  $\Delta H$  to be negative and  $\Delta E$  to be greater than  $\Delta H$   
b.  $\Delta H$  to be negative and  $\Delta E$  to be less than  $\Delta H$   
c.  $\Delta H$  to be positive and  $\Delta E$  to be less than  $\Delta H$   
d.  $\Delta H$  to be positive and  $\Delta E$  to be greater than  $\Delta H$
88. Calculate the resonance energy of  $N_2O$  from the following data:  $\Delta H_f$  of  $N_2O = 82\text{ kJ mol}^{-1}$ . Bond energies of  $N \equiv N$ ,  $N = N$ ,  $O = O$  and  $N = O$  bonds are  $946$ ,  $418$ ,  $498$  and  $607\text{ kJ mol}^{-1}$  respectively.

## 4.40 ■ Energetics

- a.  $-88 \text{ kJ mol}^{-1}$       b.  $-170 \text{ kJ mol}^{-1}$   
 c.  $-82 \text{ kJ mol}^{-1}$       d.  $-258 \text{ kJ mol}^{-1}$

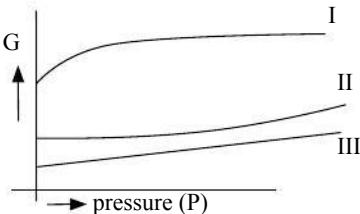
89. The enthalpy changes for the following processes are listed below



Given that the standard states for iodine and chlorine are  $\text{I}_2(\text{s})$  and  $\text{Cl}_2(\text{g})$ , the standard enthalpy of formation for  $\text{ICl}(\text{g})$  is

- a.  $-14.6 \text{ kJ mol}^{-1}$       b.  $-16.8 \text{ kJ mol}^{-1}$   
 c.  $+16.8 \text{ kJ mol}^{-1}$       d.  $+244.8 \text{ kJ mol}^{-1}$

90. The following curve represents the variation of Gibbs function 'G' with pressure at constant temperature.



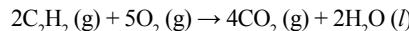
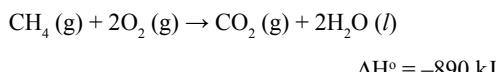
Correct match of given plots with the physical state of a substance is

- a. I – solid, III – gas, II – liquid  
 b. I – gas, II – liquid, III – solid  
 c. I – liquid, II – solid, III – gas  
 d. III – gas, II – solid, I – liquid

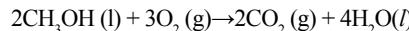
91. Which of the following is in accord with the three laws of thermodynamics?

- (I) The entropy of the universe never decreases.  
 (II) A non-spontaneous process can occur if it is coupled to a process that is sufficiently spontaneous.  
 a. I is true and II is false.  
 b. I is false and II is true.  
 c. Both I and II are true.  
 d. Both I and II are false.

92. Which of  $\text{CH}_4(\text{g})$ ,  $\text{C}_2\text{H}_2(\text{g})$  and  $\text{CH}_3\text{OH}(\text{l})$  provides the most energy per gram upon combustion and which provides the least?



$$\Delta H^\circ = -2599 \text{ kJ}$$



$$\Delta H^\circ = -1453 \text{ kJ}$$

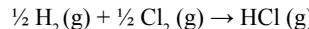
a.  $\text{C}_2\text{H}_2$  provides the most energy per gram and  $\text{CH}_3\text{OH}$  the least.

b.  $\text{C}_2\text{H}_2$  provides the most energy per gram and  $\text{CH}_4$  the least.

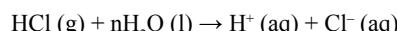
c.  $\text{CH}_4$  provides the most energy per gram and  $\text{C}_2\text{H}_2$  the least.

d.  $\text{CH}_4$  provides the most energy per gram and  $\text{CH}_3\text{OH}$  the least.

93. Calculate  $\Delta H_f^\circ$  for chloride ion from the following data:



$$\Delta H^\circ_f = -92.4 \text{ kJ}$$



$$\Delta H_{298}^\circ = -74.8 \text{ kJ}$$

$$\Delta H_f^\circ[\text{H}^+] = 0.0 \text{ kJ}$$

- a.  $-189 \text{ kJ}$       b.  $-167 \text{ kJ}$   
 c.  $+167 \text{ kJ}$       d.  $-191 \text{ kJ}$

94. The signs of  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  at  $25^\circ\text{C}$  are shown below for three reactions.

Reaction	$\Delta G$	$\Delta H$	$\Delta S$
I.	–	+	+
II.	–	–	+
III.	–	–	–

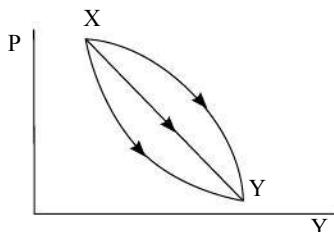
Which reaction could go in the reverse direction at high temperature?

- a. II only      b. III only  
 c. I and II      d. II and III

95. The heat liberated on complete combustion of 7.8 g benzene is 327 kJ. This heat was measured at constant volume and at  $27^\circ\text{C}$ . Calculate the heat of combustion of benzene at constant pressure ( $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$ )

- a.  $-3274 \text{ kJ mol}^{-1}$       b.  $-1637 \text{ kJ mol}^{-1}$   
 c.  $-3270 \text{ kJ mol}^{-1}$       d.  $-3637 \text{ kJ mol}^{-1}$

96. A given masss of gas expands from the state  $\times$  to the staste Y by three paths 1, 2 and 3 as shown I in the figure. If  $w_1$  and  $w_2$  and  $w_3$  respectively be the work done by the gas along three paths then:

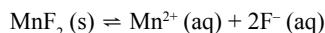


- 96.**
- $w_1 > w_2 > w_3$
  - $w_2 < w_1 < w_3$
  - $w_1 = w_2 = w_3$
  - $w_1 < w_2 < w_3$
- 97.** Calculate  $\Delta G^\circ$  for the reaction below and tell whether it is spontaneous or non-spontaneous under standard conditions at  $25^\circ\text{C}$ .
- $$2\text{S}(\text{s}) + 3\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2\text{SO}_4(\text{l})$$
- $$\Delta H^\circ = -1056 \text{ kJ/mol}$$
- $$\Delta S^\circ = -505 \text{ J/mol}$$
- $\Delta G^\circ = -906 \text{ kJ}$  and the process is spontaneous
  - $\Delta G^\circ = -1206 \text{ kJ}$  and the process is spontaneous
  - $\Delta G^\circ = -906 \text{ kJ}$  and the process is non-spontaneous
  - $\Delta G^\circ = -1206 \text{ kJ}$  and the process is non-spontaneous
- 98.** Generally, alkali metals form their oxides by an average increment of  $6 \text{ kJ mol}^{-1} \text{ K}^{-1}$  in their entropies. If at  $25^\circ\text{C}$ ,  $\Delta G_f^\circ$  of  $\text{Al}_2\text{O}_3(\text{s}) = -1582 \text{ kJ mol}^{-1}$ ;  $\Delta H_f^\circ$  of  $\text{Li}_2\text{O}(\text{s}) = 1244 \text{ kJ}$  and  $\Delta H_f^\circ$  of  $\text{Na}_2\text{O}(\text{s}) = 1411 \text{ kJ}$ . The aluminium oxide can be reduced to Al metal by
- Lithium
  - Sodium
  - Both (a) and (b)
  - None of these
- 99.** For the reaction,
- $$\text{A(g)} + 2\text{B(g)} \rightarrow 2\text{C(g)} + 3\text{D(g)}$$
- The value of  $\Delta H$  at  $27^\circ\text{C}$  is 19.0 kcal. The value of  $\Delta E$  for the reaction would be  
(given  $R = 2.0 \text{ cal K}^{-1} \text{ mol}^{-1}$ )
- 20.8 kcal
  - 19.8 kcal
  - 18.8 kcal
  - 17.8 kcal
- 100.** Determine  $\Delta H$  and  $\Delta E$  for reversible isothermal evaporation of 90 g of water at  $100^\circ\text{C}$ . Assume that water vapour behaves as an ideal gas and heat of evaporation of water is 540 cal  $\text{g}^{-1}$  ( $R = 2.0 \text{ cal mol}^{-1} \text{ K}^{-1}$ )

- a.** 48600 cal, 44870 cal  
**b.** 43670 cal, 47700 cal  
**c.** 47700 cal, 43670 cal  
**d.** 44870 cal, 48670 cal
- 101.** If work done by a gas is 144.5 J when heat given to the gas in isobaric process is 506 J. then the gas is
- $\text{SO}_2$
  - $\text{NH}_3$
  - He
  - $\text{O}_2$
- 102.** A process is carried out at constant pressure. Given that  $\Delta H$  is negative and  $\Delta E$  is less than  $\Delta H$ ,
- The system loses heat and contracts during the process
  - The system loses heat and expands during the process
  - The system absorbs heat and expands during the process
  - The system absorbs heat and contracts during the process
- 103.**  $\Delta G^\circ$  for the reaction,  $x + y \leftrightarrow z$  is  $-4.606 \text{ kcal}$ . The value of equilibrium constant of the reaction at  $227^\circ\text{C}$  is.
- 0.01
  - 100
  - 2
  - 10
- 104.** Assume a heteronuclear diatomic molecule, AB, forms a one dimensional crystal by lining up along the X-axis. Also assume that each molecule can only have one of six possible orientations, corresponding to atom A facing in either the positive or negative direction along the X-, Y-, or Z-axis. If the molecules are arranged randomly in the six directions, the molar entropy at absolute zero should be
- zero
  - $R \ln 60$
  - $R \ln 6$
  - $R \ln 6^6$
- 105.** P-V plot for two gases (assuming ideal) during adiabatic process are given in the fig. Plot X and plot Y should correspond respectively to:
- 
- He and  $\text{H}_2$
  - $\text{H}_2$  and He
  - $\text{Cl}_2$  and  $\text{H}_2$
  - $\text{H}_2$  and  $\text{Cl}_2$

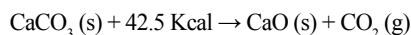
## 4.42 ■ Energetics

- 106.** The solubility of manganese (II) fluoride in water is 6.6 g/ml at 40°C and 4.8 g/litre at 100°C. Based on this data, what is the sign of  $\Delta H^\circ$  and  $\Delta S^\circ$  for the following process?



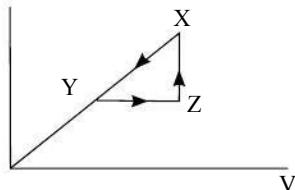
- a.  $\Delta H^\circ$  is negative and  $\Delta S^\circ$  is positive
- b.  $\Delta H^\circ$  is negative and  $\Delta S^\circ$  is negative
- c.  $\Delta H^\circ$  is positive and  $\Delta S^\circ$  is positive
- d.  $\Delta H^\circ$  is positive and  $\Delta S^\circ$  is negative

- 107.** For the system represented by the equation



- a. the reaction is exoenergetic
- b. the size of  $\Delta E$  is negative
- c. the net energy flow is from the system to the environment
- d. the internal chemical energy of one mole  $\text{CaCO}_3$  (s) is less than that of [one mole  $\text{CaO}$  (s) + one mole  $\text{CO}_2$  (g)]

- 108.** P



- (I)  $Q_X \rightarrow Y = (-)$  ve
  - (II)  $\Delta U_Y \rightarrow Z = (+)$  ve
  - (III)  $\Delta U_Z \rightarrow X = (-)$  ve
  - (IV)  $W_{ZXY} = (-)$  ve.
- a. I, II, III
  - b. I, II, IV
  - c. I, III, IV
  - d. II, III, IV

- 109.** Consider these two statements.

- (i) The reversible work done by 2 moles of an ideal gas, isothermally at 300 k, as it expands from 10 atm to 1 atm. pressure is roughly 2.764 k. cal.
  - (ii) 2 moles of a gas expand against a constant pressure of 1 atm, the change in the volume being 82.12 ml. The work done by the gas is roughly 3 cal.
- a. (i) and (ii) are correct
  - b. (i) and (ii) are incorrect

- c. (i) is incorrect, (ii) is correct

- d. (i) is correct, (ii) is incorrect

- 110.** The reversible adiabatic expansion of an ideal monatomic gas, the final volume is 10 times to the initial volume. The ratio

Final temperature  
Initial temperature is

- a.  $(1/10)^{0.666}$
- b.  $10^{1.666}$
- c.  $10^{0.666}$
- d.  $(1/10)^{1.666}$

- 111.** 4.8 g of C (diamond) on complete combustion evolves 1584 kJ of heat. The standard heat of formation of gaseous carbon is 725 kJ/mol. The energy required for the process

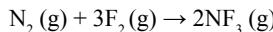
- (i)  $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{gas})$
- (ii)  $\text{C}(\text{diamond}) \rightarrow \text{C}(\text{gas})$  are

- a. 725, 723
- b. 725, 727
- c. 727, 725
- d. None of these

- 112.** Bond dissociation enthalpy of  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$  are 434, 242 and 431 kJ mol<sup>-1</sup> respectively. Enthalpy of formation of  $\text{HCl}$  is

- a. -93 kJ mol<sup>-1</sup>
- b. 245 kJ mol<sup>-1</sup>
- c. 93 kJ mol<sup>-1</sup>
- d. -245 kJ mol<sup>-1</sup>

- 113.** Consider the reaction:



$$\Delta H^\circ = -249 \text{ kJ} \text{ and } \Delta S^\circ = -278 \text{ JK}^{-1} \text{ at } 25^\circ\text{C}$$

Calculate  $\Delta G^\circ$  and state whether the equilibrium composition should favour reactants or products at standard conditions.

- a.  $\Delta G^\circ = -166 \text{ kJ}$ ; the equilibrium composition should favour reactants.
- b.  $\Delta G^\circ = -166 \text{ kJ}$ ; the equilibrium composition should favour products.
- c.  $\Delta G^\circ = -322 \text{ kJ}$ ; the equilibrium composition should favour products.
- d.  $\Delta G^\circ = -166 \text{ kJ}$ ; the equilibrium composition should favour reactants.

- 114.** Which provides the greatest increase in entropy?

- a.  $\text{H}_2\text{O}(\text{l}, 0^\circ\text{C}) \rightarrow \text{H}_2\text{O}(\text{l}, 25^\circ\text{C})$
- b.  $\text{H}_2\text{O}(\text{s}, 0^\circ\text{C}) \rightarrow \text{H}_2\text{O}(\text{l}, 0^\circ\text{C})$
- c.  $\text{H}_2\text{O}(\text{l}, 100^\circ\text{C}) \rightarrow \text{H}_2\text{O}(\text{g}, 100^\circ\text{C})$
- d.  $\text{H}_2\text{O}(\text{g}, 0.1^\circ\text{C}) \rightarrow \text{H}_2\text{O}(\text{s}, 0.1^\circ\text{C})$

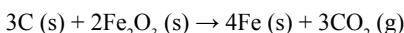
**115.** Consider these two statements.

- (I) The reversible work done by 2 moles of an ideal gas, isothermally at 300 K, as it expands from 10 atm to 1 atm, pressure is roughly 2.764 k. cal.
  - (II) 2 moles of a gas expand against a constant pressure of 1 atm, the change in the volume being 82.12 ml. The work done by the gas is roughly 3 cal.
- a. (i) and (ii) are correct  
 b. (i) and (ii) are incorrect  
 c. (i) is incorrect, (ii) is correct  
 d. (i) is correct, (ii) is incorrect

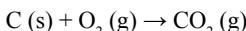
**116.** Standard free energies of formation (in kJ/mol) at 298 K are -237.2, -394.4 and -8.2 for H<sub>2</sub>O(l), CO<sub>2</sub>(g) and pentane (g) respectively. The value of E<sub>cell</sub><sup>o</sup> for the pentane-oxygen fuel cell is:

- a. 1.0968 V      b. 0.0698 V  
 c. 1.968 V      d. 2.0968 V

Given that



$$\Delta H^\circ = -93657 \text{ kcal at } 25^\circ\text{C}$$



$$\Delta H^\circ = -94050 \text{ kcal at } 25^\circ\text{C}$$

The value of ΔH°(Fe<sub>2</sub>O<sub>3</sub>) is

- a. -19.650 kcal      b. -196.5 kcal  
 c. 93.657 kcal      d. -286.4 kcal

**117.** The enthalpy of solution of BaCl<sub>2</sub>(s) and BaCl<sub>2</sub>.2H<sub>2</sub>O(s) are -20.6 and 8.8 kJ mol<sup>-1</sup> respectively. The enthalpy change for the hydration of BaCl<sub>2</sub>(s) is

- a. 29.8 kJ      b. -11.8 kJ  
 c. -20.6 kJ      d. -29.4 kJ.

**118.** The heat of formation of CO<sub>2</sub> is -409 kJ/mol. The energy required for the process



- a. Is equal to 1227 kJ  
 b. Less than 1227 kJ  
 c. More than 1227 kJ  
 d. Cannot be predicted

**119.** Calculate Q and W for the isothermal reversible expansion of one mole of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K.

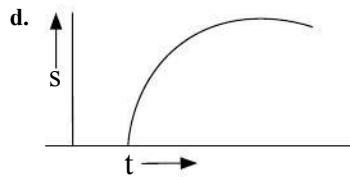
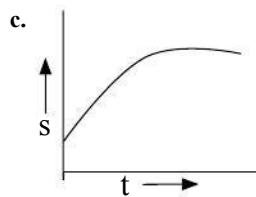
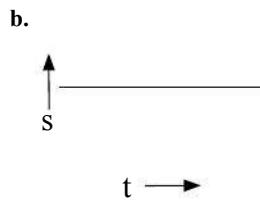
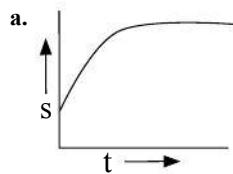
- a. 5.22 kJ, -5.22 kJ

- b. -27.3 kJ, 27.3 kJ  
 c. 27.3 kJ, -27.3 kJ  
 d. -5.22 kJ, 5.22 kJ

**120.** Calculate the heat of combustion of methane at constant volume. The thermal capacity of the calorimeter system is 177 kJ K<sup>-1</sup> (R = 8.314 J K<sup>-1</sup> mol<sup>-1</sup>)

- a. -695 kJ mol<sup>-1</sup>      b. -1703 kJ mol<sup>-1</sup>  
 c. -890 kJ mol<sup>-1</sup>      d. -885 kJ mol<sup>-1</sup>

**121.** If a copper block of mass m at temperature 'T1' is kept in the open atmosphere at temperature 'T2' and T<sub>2</sub> > T<sub>1</sub>. The variation of entropy of the copper block with time can be best illustrated by which of these graph.



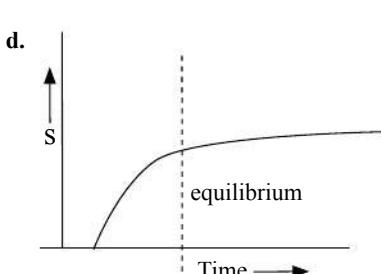
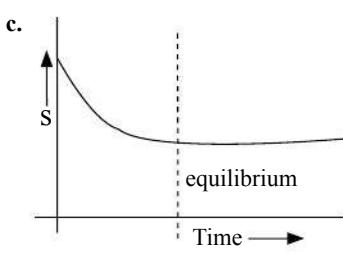
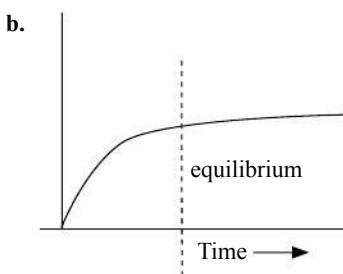
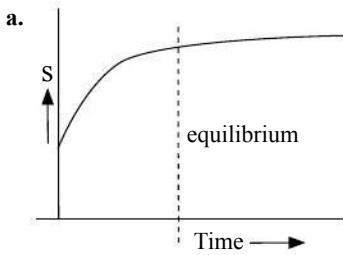
**122.** The lattice energy of NaCl is 780 kJ mol<sup>-1</sup>. The enthalpies of hydration of Na<sup>+</sup>(g) and Cl<sup>-</sup>(g) ions are -406 kJ mol<sup>-1</sup> and -364 kJ mol<sup>-1</sup>. The enthalpy of solution of NaCl(s) is

- a. 10 kJ mol<sup>-1</sup>      b. -10 kJ mol<sup>-1</sup>  
 c. 736 kJ mol<sup>-1</sup>      d. 100 kJ mol<sup>-1</sup>

**124.** The enthalpy (heat) of formation of water is 286 kJ mole<sup>-1</sup>. From this it can be concluded that

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- a. the enthalpy change when 1 g of hydrogen is burnt in oxygen is  $-286 \text{ kJ}$
  - b. there is a decrease in the enthalpy of the system when water is formed
  - c. the mean bond dissociation energy of O-H is  $143 \text{ kJ mol}^{-1}$ .
  - d. the enthalpy change for the reaction  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(l)$  is  $-286 \text{ kJ mol}^{-1}$
125. Which of these correctly represents the entropy (s) of an isolated system during a process?



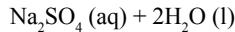
## Multiple Correct Answer Type Questions

126. Which of the following statement is/are correct?
- From the following reaction  
 $\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}), \Delta H = q_1$   
Heat of formation of  $\text{CO}_2(\text{g})$  is  $q_1$
  - From the following reaction  
 $\text{C}(\text{graphite}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g}), \Delta H = q_2$   
Heat of combustion of carbon is  $q_2$ .
  - From the above reaction, heat of combustion of  $\text{CO}(\text{g})$  is  $q_1$  and that of carbon is  $q_1 + q_2$ .
  - From the above reaction, heat of formation of  $\text{CO}_2(\text{g})$  is  $q_1 + q_2$ .
127. Which of the following statements is/are true?
- A highly spontaneous process need not occur rapidly
  - A non spontaneous process cannot be caused to occur.
  - The reverse of a spontaneous reaction is always non spontaneous.
  - A spontaneous process always moves towards equilibrium.
128.  $C_p - C_v = R$ . This R is not equal to:
- Change in rotational energy
  - Change in KE
  - Change in PE
  - Work done which system can do on expanding the gas per mol per degree increase in temperature.
129. For which of the following reaction is the standard entropy of reaction  $\Delta S^\circ$  positive?
- $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$
  - $2\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$
  - $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{g})$
  - $\text{C}_2\text{H}_5\text{OH}(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g})$
130. The enthalpy change for a reaction depend upon the
- physical state of reactants and products
  - use of different reactants for the same product
  - nature of intermediate reaction steps
  - difference in initial or final temperatures of involved substances
131. Which of the following always increase with increase in temperature?

- a. pressure of the gas at constant volume  
 b. solubility of gas  
 c. entropy  
 d. rate of reaction
132. Which of the following is/are spontaneous process?  
 a.  $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$  if  $p_{\text{NH}_3} = 1 \text{ atm}$ ,  $p_{\text{H}_2} = P_{\text{N}_2} = 0$  and  $K_p = 2 \times 10^{-6}$   
 b.  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$  if  $p_{\text{H}_2} = P_{\text{N}_2} = 1 \text{ atm}$ ,  $p_{\text{NH}_3} = 0$  and  $K_p = 4 \times 10^5$   
 c. the expansion of gas into a vacuum  
 d. dissolving more solute in a saturated solution
133. Internal energy and entropy are state functions  
 a. internal energy (U) is a state function and  $\Delta U$  is independent of path.  
 b. In a cyclic process:  $\Delta S = 0$  but  $\Delta U \neq 0$   
 c. Cv values of H<sub>2</sub> and He are equal at all temperatures  
 d. q and w are path dependent
134. For which of the following processes will the entropy decrease?  
 a. Reaction of magnesium with oxygen to form magnesium oxide.  
 b. Reaction of nitrogen and hydrogen to form ammonia.  
 c. Sublimation of dry ice.  
 d. Condensation of steam.
135. Which of the following statements must be true for the entropy of a pure solid to be zero?  
 a. Temperature must be 0 K.  
 b. The solid must be perfectly ordered  
 c. The solid must be an element.  
 d. The solid must be crystalline, not amorphous
136. For an ideal gas undergoing isothermal and reversible process  
 a.  $\Delta U$  and  $\Delta H$  both are zero  
 b.  $\Delta U = 0$  but  $\Delta H \neq 0$   
 c.  $\Delta S$  is +ve during expansion and -ve during compression  
 d.  $\Delta S = 0$  and  $\Delta U = 0$
137. In certain chemical process both  $\Delta H$  and  $\Delta S$  have values greater than zero. Under what conditions, the reaction would not be spontaneous?  
 a.  $\Delta H > T\Delta S$   
 b.  $\Delta H < T\Delta S$   
 c.  $\Delta G > 0$   
 d.  $\Delta G < 0$
138. Which statement is/are not true about the standard states of F<sub>2</sub>(g) and C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>(aq)?  
 a. The standard state for F<sub>2</sub>(g) is the pure gas at 1 atm and for C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>(aq) is the solution at a concentration of 1 mol/L.  
 b. The standard state for F<sub>2</sub>(g) is the pure gas at 1 mol/L and for C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>(aq) is the solution at a concentration of 1 mol/L.  
 c. The standard state for F<sub>2</sub>(g) is the pure gas at 1 atm and for C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>(aq) is the pure solid at 1 atm.  
 d. The standard state for F<sub>2</sub>(g) is the pure gas at 1 mol/L and for C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>(aq) is the pure solid at atm.
139. The heat evolved during the combustion of 46 gm of ethanol in a bomb calorimeter was determined to be 670.5 kcal/mol at 25°C. The value of  $\Delta U$  of the reaction at the same temperature is  
 a. -335.25 Kcal      b. -660.3 Kcal  
 c. -670.5 Kcal      d. -2802.6 kJ
140. Which of the following process/es proceed towards more disordered state?  
 a. sublimation of dry ice  
 b. crystallization of salt from solution  
 c. dissolution of sugar in water  
 d. stretching of the rubber
141. Identify the incorrect statement/s regarding entropy.  
 a. at absolute zero temperature, entropy of perfectly crystalline substance is taken to zero  
 b. at absolute zero temperature, the entropy of perfectly crystalline substance is positive  
 c. at 0°C the entropy of perfectly crystalline substance is positive  
 d. at absolute zero temperature, the entropy of all crystalline substances is taken to be zero
142. xy, x<sub>2</sub> and y<sub>2</sub> are diatomic molecules if  $\Delta H_{x-x}$ ,  $\Delta H_{y-y}$  and  $\Delta H_{xy}$  are in the ratio of 2 : 1 : 2 and enthalpy of formation of x - y form x<sub>2</sub> and y<sub>2</sub> is -100 kJ/mol. The value of  $\Delta H_x - x$  is  
 a. 47.85 Kcal/mol  
 b. 23.92 Kcal/mol  
 c. 100 kJ/mol  
 d. 200 Kcal/mol
143. Which of the following statement is/are true?  
 a. work is a state function  
 b. temperature is a state function  
 c. change in the state is completely defined when the initial and final state are specified  
 d. all of them

## 4.46 ■ Energetics

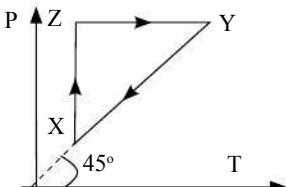
- 144.** Which of the following is/are true?
- A spontaneous process is one that can proceed on its own.
  - The reverse of a non-spontaneous process is always spontaneous.
  - A spontaneous process need not occur immediately.
  - A spontaneous process must be exothermic and must have an increase in entropy.
- 145.** Which of the following expression is correct for an adiabatic process?
- $(T_2/T_1) = (V_1/V_2)^{\gamma-1}$
  - $P_2/P_1 = (T_1/T_2)^{\gamma-1/\gamma}$
  - $P_2 V_2^\gamma = P_1 V_1^\gamma$
  - $P_1 V_1^{\gamma-1} = P_2 V_2^{\gamma-1}$
- 146.** For which change  $\Delta H = \Delta E$
- $H_2 + I_2 \leftrightarrow 2HI$
  - $HCl + NaOH \rightarrow NaCl + H_2O$
  - $C(s) + O_2(g) \leftrightarrow CO_2(g)$
  - $N_2 + 3H_2 \rightarrow 2NH_3$
- 147.** Which statement is/ are not true about the formation of  $CaCO_3(s)$  from  $CaO(s)$  and  $CO_2(g)$  at 1.00 atm?
- $$CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$$
- $$\Delta H^\circ = -178.7 \text{ kJ and } \Delta S^\circ = -150.4 \text{ JK}^{-1}$$
- The reaction is spontaneous at low temperature.
  - The reaction is spontaneous at all temperatures.
  - The reaction is not spontaneous at any temperature
  - The reaction is spontaneous at high temperatures.
- 148.** The correct statement/s among the following is/are
- mass plus energy of the universe remains always constant while entropy of the universe remains increasing continuously
  - an exothermic reaction with  $\Delta S$  being positive, will be spontaneous only at high temperature
  - in a reversible process, the system always in equilibrium with surroundings
  - in any cyclic process  $\Delta X = 0$  where X is a state function.
- 149.** Which of the following reaction is exothermic?
- $C(\text{diamond}) \rightarrow C(\text{graphite})$
  - $C_2H_6 \rightarrow C_2H_4 + H_2$
  - $C_2H_6 + 7/2 O_2 \rightarrow 2CO_2 + 3H_2O(l)$
  - $2NaOH(aq) + H_2SO_4(aq) \rightarrow$
- 150.** For which reaction change of entropy will be negative?
- $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
  - $MgO_{(s)} + H_{2(g)} \rightleftharpoons Mg_{(g)} + H_2O_{(l)}$
  - $NH_4NO_{3(s)} \rightleftharpoons N_2O_{(g)} + 2H_2O_{(g)}$
  - $HCl_{(g)} + NH_3_{(g)} \rightleftharpoons NH_4Cl_{(s)}$
- 151.** The correct statement amongst the following is/are
- at equilibrium  $\Delta H_{S,P} = 0$
  - the condition of equilibrium at constant P and T is that G must be minimum
  - at equilibrium  $\Delta G_{P,T} = 0$
  - $\Delta G^\circ$  calculated using the equation;  $\Delta G^\circ = -RT \ln K_p$ , is the free energy change of the reaction when each of the species (reactants and products) is in the standard state of unit activity that is, roughly unit concentration.
- 152.** Correct statement among the following is/are
- mass plus energy of the universe remains always constant while entropy of the universe remains increasing continuously
  - an exothermic reaction with  $\Delta S$  being positive, will be spontaneous only at high temperature
  - in a reversible process the system always in equilibrium with surroundings
  - in any cyclic process  $\Delta X = 0$  where Xs a state function.
- 153.** The enthalpy change for a reaction depends upon:
- The differences in initial or final temperatures of involved substances
  - The nature of intermediate reaction steps
  - Use of different reactants for the same product
  - The physical states of reactants and products
- 154.** Which of the following is/are correct?
- Numerical value of  $\Delta H$  is less than that of  $\Delta E$  for the reaction  $C(s) + \frac{1}{2}O_2(g) \rightleftharpoons CO(g)$
  - In an exothermic reaction, the enthalpy of products is less than that of the reactants
  - $\Delta H(\text{fusion}) = \Delta H(\text{sub}) - \Delta H(\text{vap})$
  - A reaction for which  $\Delta H^\circ < 0$  and  $\Delta S^\circ > 0$  is possible at all temperatures.
- 155.** Among the following, the state function(s) is/are
- Internal energy
  - Irreversible expansion work
  - Reversible expansion work
  - Molar enthalpy



## Linked-Comprehension Type Questions

### Comprehension 1

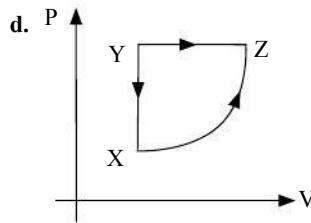
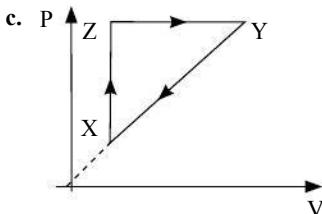
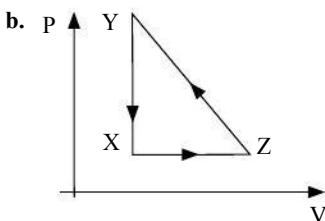
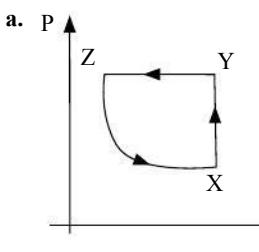
A cyclic process XYZX is shown in figure. The process is for 2 mole of monatomic gas. As the gas behaves ideally. So one can apply  $PV = nRT$  for the gas. The work done by the gas in a process is given as  $W = \int PdV$



156. The process  $X \rightarrow Y$  is isochoric. The volume of the gas numerically in this process is

- a.  $3R$
- b.  $3R$
- c.  $5/2 R$
- d.  $2R$

157. The same cyclic process in the PV – diagram is



158. During the process  $X \rightarrow Y$ , The internal energy of the gas

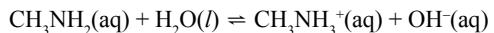
- a. Depends on volume
- b. Decreases
- c. Increases
- d. Does not change

### Comprehension 2

The values of  $\Delta H$  and  $\Delta S$  generally do not vary much with temperature. As a consequence, the dependence of  $\Delta G$  with temperature is governed mainly by the value of  $T$  in the expression  $\Delta G = \Delta H - T\Delta S$ . The entropy term –  $T\Delta S$  has the greater effect on the spontaneity of the process.

Under non-standard conditions,  $\Delta G$  is related to  $\Delta G^\circ$  and the value of the reaction quotient,  $Q : \Delta G = \Delta G^\circ - RT \ln Q$ . At equilibrium ( $\Delta G = 0$ ,  $Q = K$ ),  $\Delta G^\circ = -RT \ln K$

159. If the value of equilibrium constant for the reaction given below is  $4.4 \times 10^{-4}$  at 298 K.



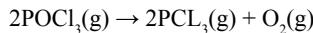
Find  $\Delta G^\circ$  for this reaction.

- a.  $-38.28 \text{ kJ}$
- b.  $-19.14 \text{ kJ}$
- c.  $-9.57 \text{ kJ}$
- d. Zero

160. Find the value of  $\Delta G$  when  $[\text{H}^+] = 3.0 \times 10^{-10} \text{ M}$ ,  $[\text{CH}_3\text{NH}_3^+] = 8.0 \times 10^{-3} \text{ M}$ , and  $[\text{CH}_3\text{NH}_2] = 0.070 \text{ M}$ .

- a.  $+11.8$
- b.  $-5.9$
- c.  $-10.8$
- d.  $-11.8$

161. A particular reaction given below can be spontaneous if



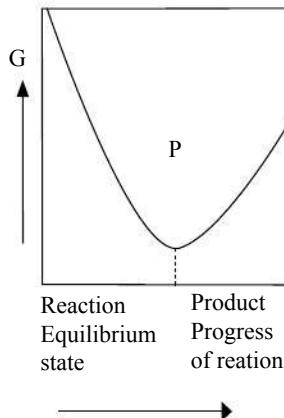
$$\Delta H^\circ = 572 \text{ kJ}; \Delta S^\circ = 179 \text{ J/K}$$

## 4.48 ■ Energetics

- a. T > 1200 K
- b. T > 1600 K
- c. T > 2400 K
- d. T > 3200 K

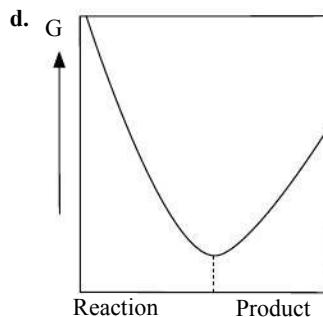
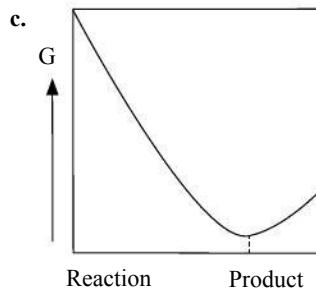
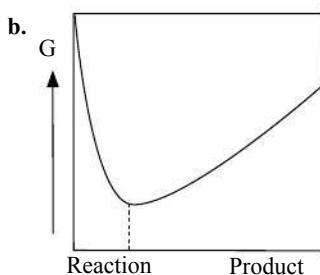
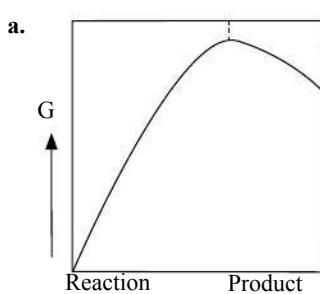
### Comprehension 3

For a reversible reaction at constant temperature and at constant pressure the equilibrium composition of reaction mixture corresponds to the lowest point on Gibbs energy Vs progress of reaction diagrams as shown. At equilibrium, Gibbs energy of reaction ( $\Delta G$ ) is equal to zero.



162. The value of  $\log_{10} k_{eq}$  (equilibrium constant) can be given as
- a.  $\frac{\Delta G^\circ}{RT}$
  - b.  $\frac{T\Delta S^\circ - \Delta H^\circ}{2.303RT}$
  - c.  $\frac{\Delta H^\circ - T\Delta S^\circ}{2.303 RT}$
  - d.  $\frac{2.303 RT}{T\Delta S^\circ - \Delta H^\circ}$

163. Which diagram represents the large value of equilibrium constant for the reversible reaction?



164. The temperature dependence of the equilibrium constant can be given by the equation

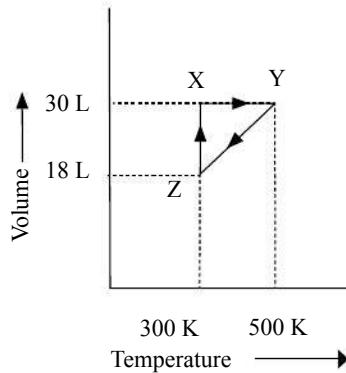
a.  $\ln K = \frac{\Delta H^\circ}{R} \left( \frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$

b.  $\ln K = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$

c.  $\ln K = \frac{\Delta G^\circ}{R} \left( \frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$

d.  $\ln K = -\frac{\Delta G^\circ}{R} (T) + \frac{\Delta S^\circ}{R}$

### Comprehension 4



Answer the following questions based on the given diagram:

- 165.** Process , X → Y represents  
 a. Isobaric                    b. isochoric  
 c. isothermal                d. adiabatic
- 166.** The pressure at Z is  
 a. 3.518 atm                b. 1.368 atm  
 c. 0.0821 atm              d. 0.821 atm
- 167.** The process which occurs in going from, Y → Z is  
 a. isothermal                b. adiabatic  
 c. isochoric                 d. isobaric

### Comprehension 5

Entropy is a measurement of randomness or disorder of any system. When a liquid is converted to the vapour state entropy of the system increases. Entropy in any of the phase transformation can be calculated by using this relation  $\Delta S = \Delta H/T$ .

In a reversible adiabatic process  $\Delta S$  is zero. The rise in temperature in isobaric or isochoric process increases the randomness of system and it can be given by

$$\Delta S = 2.303n C \log_{10} \frac{T_2}{T_1}$$

Here  $C = C_p$  or  $C_v$

- 168.** The element gallium, Ga, freezes at 2.8°C, and its enthalpy of fusion is  $\Delta H_{fus} = 5.59 \text{ kJ/mol}$ . Calculate the value of  $\Delta S$  for the freezing of 90.0 g of Ga(l) at 29.8°C.  
 a. 47.6 J/K                b. 23.8 J/K  
 c. 4.76 J/K                d. 32.86 J/K
- 169.** Write the correct sequence of entropy change when a solid melt, a gas liquefies, liquid vapourizes and a solid dissolves in water.  
 a. Increases, increases, increases, increases respectively  
 b. Increases, decreases, increases, decreases respectively  
 c. Increases, decreases, increases, increases respectively  
 d. Decreases, increases, decreases, increases respectively
- 170.** Find the entropy change when 0.5 M of an ideal gas expands at a constant temperature from an initial volume of 10 L to a final volume of 75 L.  
 a. 8.376 J/K                b. 4.188 J/K  
 c. 16.752 J/K              d. 7.367 J/K

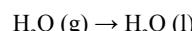
### Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given. Mark

- a. if A and R both are correct and R is the correct explanation of A;
- b. if A and R both are correct but R is not the correct explanation of A;
- c. A is true but R is false;
- d. A is false but R is true,
- e. both A and R are false.

- 171.** (A): The enthalpy of formation of  $\text{H}_2\text{O}(l)$  is greater than that of  $\text{H}_2\text{O}(g)$ .

(R): Enthalpy change is -ve for the condensation reaction,



- 172.** (A):  $C_p - C_v = R$  for ideal gas

(R):  $(dU/dV)_T = 0$  for ideal gas

- 173.** (A): All combustion reactions are exothermic.

(R): Products are more stable than reactants in exothermic process.

- 174.** (A): Chlorine when tried to be solidified does not have zero entropy when at absolute zero.

(R): Chlorine contains a mixture of isotopes and is difficult to solidify.

- 175.** (A): Heat of neutralization of HF is more than that of HCl by NaOH.

(R): HCl is stronger acid than HF.

- 176.** (A): The thermodynamic function which determines the spontaneity of a process is the free energy, for a process to be spontaneous, the change in free energy must be negative.

(R): The change in free energy is related to the change in enthalpy and change in entropy. The change in entropy for a process must be always positive if it is spontaneous.

- 177.** (A): All exothermic reactions are spontaneous at room temperature.

(R): In  $(\Delta G = \Delta H - T\Delta S)$ ,  $\Delta G$  becomes negative and negative sign of  $\Delta G$  indicates spontaneous reaction.

- 178.** (A): Endothermic reaction is spontaneous at all temperatures.

(R):  $\Delta G$  is negative when  $T\Delta S > \Delta H$

- 179.** (A): As temperature increases, heat of reaction also increases for exothermic as well for endothermic reactions.

## 4.50 ■ Energetics

(R):  $\Delta H$  varies with temperatures as given by

$$\Delta H_2 \text{ (at } T_2) = \Delta H_1 \text{ (at } T_1) + \Delta C_p (T_2 - T_1)$$

180. (A): Efficiency of a reversible engine is maximum (100%) when temperature of the sink is  $-273^{\circ}\text{C}$  ( $T_1$ )

$$(R): \eta \text{ (efficiency)} = \frac{T_2 - T_1}{T_2}$$

181. (A): As solid changes to liquid and then to vapour state, entropy increases.

(R): As going from solid to liquid and then to vapour state, disorder increases.

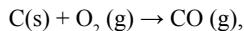
182. (A): In the case of an ideal gas, the changes in Gibbs and Helmholtz free energies are equal to each other ( $\Delta G = \Delta A$ ) for isothermal reversible processes.

(R): There is no change in internal energies and enthalpies for ideal gases at constant temperature.

183. (A): When  $\text{H}_2\text{O}$  is added to  $\text{CaO}$ , heat is liberated.

(R): Reaction between  $\text{CaO}$  and  $\text{H}_2\text{O}$  is exothermic.

184. (A): In the following reaction

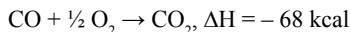


$$\Delta H = \Delta E - RT$$

(R):  $\Delta H$  is related to  $\Delta E$  by equation

$$\Delta H = \Delta E + \Delta n_g RT$$

185. (A): In the following reaction



and thus

$$\Delta H_f(\text{CO}_2) = -68 \text{ kcal mol}^{-1}$$

(R): 1 mol of  $\text{CO}_2$  is formed and enthalpy change is the heat of formation of  $\text{CO}_2$ .

186. (A): Heat of neutralization of HF (aq), a weak acid, with NaOH (aq) is less than 13.7 kcal, in an exothermic reaction.

(R): Some heat is lost in the ionization of a weak acid.

187. (A): The standard enthalpy of formation of graphic is taken as zero but of diamond is not zero but it is equal to 1.816 kJ/mol.

(R): Among carbon allotropes, diamond is taken as standard state.

188. (A): In case of some glassy solids having mixture of isotopes, crystals of  $\text{CO}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}$  etc. entropy is not zero even at absolute zero temperature

(R): These kind of solids do not have perfect order even at absolute zero temperature.

189. (A): Enthalpy changes are positive when  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and salts like  $\text{NaCl}$ ,  $\text{KCl}$  etc. which do not form hydrates are dissolved in water. But enthalpy changes are negative when anhydrous salts capable of forming hydrates are dissolved in water.

(R): The difference in the behaviour is due to large differences in the molecular weights of hydrated and anhydrous salts. The substances with larger molecular weights usually show positive enthalpy change on dissolution.

190. (A):  $\Delta E$  is state function of the system.

(R): As it depends upon the final and initial state of the system.

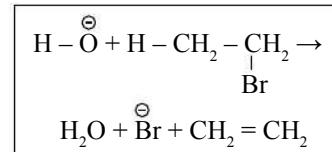
191. (A): In any reversible cycle process, the net increase in entropy of the system is zero.

(R): As  $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}}$  as in case of reversible cyclic process  $\Delta S_{\text{system}}$  is positive, but of surrounding is negative in same amount. That is why  $\Delta S_{\text{universe}} = 0$

192. (A): The enthalpy of neutralization of equivalent of HF and 1 equivalent NaOH is 14 kcal/mol. which is higher than HCl and NaOH?

(R): It is because the enthalpy of hydration of  $\text{F}^-$  is higher than that of heat enthalpy of dissociation.

193. (A): The entropy change in the reaction.



is positive

(R): Entropy increase when no. of particles or (i.e. molecules or ions) of the product or, in the product directions increases.

194. (A): The amount of work done in the isothermal expansion is greater than work done in the adiabatic system for same final volume.

(R): In the adiabatic expansion of a gas temperature and pressure both decrease due to decrease in internal energy of the system.

195. (A): There is a natural asymmetry between converting work to heat and converting heat to work.

(R): No process is possible in which the sole result in the absorption of heat from a reservoir and its complete conversion into work

### Matrix-Match Type Questions

**196.** Match the following:

- | <b>List I</b>               | <b>List II</b>                   |
|-----------------------------|----------------------------------|
| A. Cyclic process           | (p) $\Delta H$ is positive       |
| B. Spontaneous              | (q) $\Delta E = 0, \Delta H = 0$ |
| C. Endothermic              | (r) $\Delta G$ is negative       |
| D. A process in equilibrium | (s) $\Delta G = 0$               |

**197.** Match the following:

- | <b>List I</b>                                                                           | <b>List II</b>                        |
|-----------------------------------------------------------------------------------------|---------------------------------------|
| A. Reversible adiabatic compression                                                     | (p) $\Delta_{\text{Surrounding}} < 0$ |
| B. Reversible vaporization of liquid                                                    | (q) $\Delta_{\text{Surrounding}} = 0$ |
| C. $2\text{N(g)} \rightarrow \text{N}_2(\text{g})$                                      | (r) $\Delta S_{\text{system}} > 0$    |
| D. $\text{CaCO}_3(\text{s}) \xrightarrow{\Delta} \text{CaO(s)} + \text{CO}_2(\text{g})$ | (s) $\Delta S_{\text{system}} < 0$    |

**198.** Match the following:

- | <b>List I</b>                        | <b>List II</b>                                                 |
|--------------------------------------|----------------------------------------------------------------|
| A. Reversible isothermal expansion   | (p) $w = -RP_{\text{ext}} \frac{[T_2 P_1 - T_1 P_2]}{P_1 P_2}$ |
| B. Irreversible isothermal expansion | (q) $w = \frac{R}{\gamma - 1} [T_2 - T_1]$                     |
| C. Reversible adiabatic expansion    | (r) $w = -P_{\text{ext}} (V_2 - V_1)$                          |
| D. Irreversible adiabatic expansion  | (s) $w = -2.303 RT \log_{10} \frac{V_2}{V_1}$                  |

**199.** Match the following.

- | <b>List I</b>                                                                                       | <b>List II</b>                                     |
|-----------------------------------------------------------------------------------------------------|----------------------------------------------------|
| A. Ice $\rightleftharpoons \text{H}_2\text{O(l)}$ at room temperature $25^\circ\text{C}$            | (p) $\Delta H = -\text{ve}, \Delta S = +\text{ve}$ |
| B. $\text{NH}_2\text{COONH}_4(\text{s}) \rightarrow 2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$ | (q) $\Delta G = +\text{ve}$                        |
| C. $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$                                        | (r) $\Delta H = +\text{ve}, \Delta S = -\text{ve}$ |
| D. $3\text{O}_2(\text{g}) \rightarrow 2\text{O}_3(\text{g})$                                        | (s) $\Delta G = -\text{ve}$                        |

**200.** Match the following:

- | <b>List I</b>                                                                   | <b>List II</b>             |
|---------------------------------------------------------------------------------|----------------------------|
| A. Internal energy of $\text{O}_2$ gas at $0\text{ K}$ ( $-273^\circ\text{C}$ ) | (i) exothermic reaction    |
| B. heat of combustion of $\text{N}_2$                                           | (ii) $< 13.7 \text{ Kcal}$ |
| C. heat of neutralization of $\text{HCl}$ and $\text{CH}_3\text{COOH}$          | (iii) $0$                  |
| D. $2\text{CO} + \text{O}_2 \rightarrow \text{CO}_2$                            | (iv) $+\text{ve}$          |

**201.** Match the following:

- | <b>List I</b>                   | <b>List II</b>                       |
|---------------------------------|--------------------------------------|
| A. Formation of ammonia         | (p) Endothermic                      |
| B. Formation of nitric oxide    | (q) Exothermic                       |
| C. Heat of neutralization of HF | (r) $> 13.7 \text{ kcal}$            |
| D. Heat of combustion           | (s) may be exothermic or endothermic |

**202.** Match the following:

- | <b>List I</b>                                                     | <b>List II</b>                               |
|-------------------------------------------------------------------|----------------------------------------------|
| A. $\Delta S$ gas for isothermal of an ideal gas                  | (p) $nR \ln \left( \frac{P_1}{P_2} \right)$  |
| B. Work done in reversible isothermal ideal gas expansion         | (q) $-nFE$                                   |
| C. $\Delta G$ for reversible isothermal expansion of an ideal gas | (r) $nRT \ln \left( \frac{P_2}{P_1} \right)$ |
| D. $(\Delta G_{\text{system}})T, P$                               | (s) $nR \ln \left( \frac{V_2}{V_1} \right)$  |

**203.** Match the following:

- | <b>List I</b>                                      | <b>List II (Heat of neutralization)</b> |
|----------------------------------------------------|-----------------------------------------|
| A. $\text{H}_2\text{SO}_4 + \text{NaOH}$           | (p) $13.7 \text{ Kcal}$                 |
| B. $\text{H}_2\text{SO}_4 + \text{NH}_4\text{OH}$  | (q) $> 13.7 \text{ kcal}$               |
| C. $\text{CH}_3\text{COOH} + \text{NH}_4\text{OH}$ | (r) $< 13.7 \text{ kcal}$               |
| D. $\text{NaOH} + \text{HF}$                       | (s) cannot be said                      |

## 4.52 ■ Energetics

204. Match the following:

### List I

1. Exothermic substance
2. Endothermic substance
3. Heat of formation
4. Heat of combustion

### List II

- (i) Less stable
- (ii) More stable
- (iii) Exothermic
- (iv) May be exothermic or endothermic
- (v) Endothermic

### The IIT-JEE Corner

205. Molar heat capacity of water in equilibrium with ice at constant pressure is

- a. zero
- b. infinity
- c.  $40.45 \text{ J K}^{-1} \text{ mol}^{-1}$
- d.  $75.48 \text{ J K}^{-1} \text{ mol}^{-1}$

[IIT 1997]

206. Standard molar enthalpy of formation of  $\text{CO}_2$  is equal to

- a. zero
- b. the standard molar enthalpy of combustion of gaseous carbon.
- c. the sum of standard molar enthalpies of formation of CO and  $\text{CO}_2$
- d. the standard molar enthalpy of combustion of carbon (graphite)

[IIT 1997]

207. The enthalpy change involved in the oxidation of glucose is  $-2880 \text{ kJ mol}^{-1}$ . Twenty five percent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance that a person will be able to walk eating 120 g of glucose?

- a. 7.9 km
- b. 9.7 km
- c. 4.8 km
- d. 8.4 km

[IIT 1997]

208. Anhydrous  $\text{AlCl}_3$  is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution (ionization energy of Al =  $5137 \text{ kJ mol}^{-1}$ ,  $\Delta H_{\text{hydration}}$  for  $\text{Al}^{+3} = -4665 \text{ kJ mol}^{-1}$ ,  $\Delta H_{\text{hydration}}$  for  $\text{Cl}^- = -381 \text{ kJ mol}^{-1}$ )

- a. ionic
- b. covalent
- c. both
- d. none

[IIT 1997]

209. Calculate the enthalpy change for the combustion of cyclopropane at 298 K, if the enthalpy of formation  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(l)$  and propene (g) are  $-393.5$ ,  $-385.8$

and  $20.42 \text{ kJ mol}^{-1}$  respectively. The enthalpy of isomerization of cyclopropane to propene is  $-33.0 \text{ kJ mol}^{-1}$ .

- a.  $1802 \text{ kJ mol}^{-1}$
- b.  $2091 \text{ kJ mol}^{-1}$
- c.  $2196 \text{ kJ mol}^{-1}$
- d. none

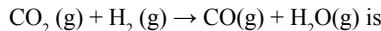
[IIT 1998]

210. Which of the following is not an endothermic reaction?

- a. combustion of methane
- b. decomposition of water
- c. dehydrogenation of ethane or ethylene
- d. conversion of graphite to diamond

[IIT 1999]

211. The  $\Delta H_f^\circ$  for  $\text{CO}_2(\text{g})$ ,  $\text{CO}(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  are  $-393.5$ ,  $-110.5$  and  $-241.8 \text{ kJ mol}^{-1}$  respectively. The standard enthalpy change (in kJ) for the reaction



- a. 524.1
- b. 41.2
- c.  $-262.5$
- d.  $-41.2$

[IIT 2000]

212. Which of the following statement is false?

- a. work is a state function
- b. temperature is a state function
- c. change of state is completely defined when initial and final states are specified.
- d. work appears at the boundary of the solution.

[IIT 2001]

213. In thermodynamics, a process is called reversible when

- a. surroundings and system change into each other
- b. there is no boundary between system and surroundings
- c. the surroundings are always in equilibrium with the system
- d. the system changes into the surroundings spontaneously

[IIT 2001]

214. One mole of a non-ideal gas undergoes a change of state  $(2.0 \text{ atm}, 3.0 \text{ L}, 95 \text{ K}) \rightarrow (4.0 \text{ atm}, 5.0 \text{ L}, 245 \text{ K})$  with a change in internal energy,  $\Delta U = 30.0 \text{ L atm}$ . The change in enthalpy ( $\Delta H$ ) of the process in L atm is

- a. 40.0
- b. 42.3
- c. 44.0
- d. not defined, because pressure is not constant

[IIT 2002]

215. Which of the following reaction defines  $\Delta H^\circ_f$ ?

- a. C (diamond) + O<sub>2</sub> (g) → CO<sub>2</sub> (g)
- b.  $\frac{1}{2}$  H<sub>2</sub> (g) +  $\frac{1}{2}$  F<sub>2</sub> (g) → HF (g)
- c. N<sub>2</sub> (g) + 3H<sub>2</sub> (g) → 2NH<sub>3</sub> (g)
- d. CO (g) +  $\frac{1}{2}$  O<sub>2</sub> (g) → CO<sub>2</sub> (g)

[IIT 2003]

216. Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre of 10 litre at 300 K. The enthalpy change (in kJ) for the process is

- a. 11.4 kJ
- b. -11.4 kJ
- c. 0 kJ
- d. 4.8 kJ.

[IIT 2004]

217. The enthalpy of vapourization of a liquid is 30 kJ mol<sup>-1</sup> and entropy of vapourization is 5 J mol<sup>-1</sup> K. The boiling point of the liquid at 1 atm is

- a. 250 K
- b. 400 K
- c. 450 K
- d. 600 K

[IIT 2004]

218. One mole of monatomic ideal gas at T (K) is expanded from 1<sub>i</sub> to 2<sub>f</sub> adiabatically under a constant external pressure of 1 atm the final temperature of the gas in Kelvin is

- a. T
- b.  $T/2^{5/3-1}$
- c.  $T - \frac{2}{3 \times 0.0821}$
- d.  $T + \frac{3}{2 \times 0.0821}$

[IIT 2005]

219. For the reaction, 2CO + O<sub>2</sub> → 2CO<sub>2</sub>,  $\Delta H = -560$  kJ. Two moles of CO and one mole of O<sub>2</sub> are taken in a container of volume 1 L. They completely form two moles of CO<sub>2</sub>, the gases deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of  $\Delta U$  at 500 K.

$$(1 \text{ L atm} = 0.1 \text{ kJ})$$

- a. 557 KJ
- b. 55.7 KJ
- c. 278 KJ
- d. 27.8 KJ

[IIT 2006]

220. The direct conversion of A to B is difficult, hence it is carried out by the following shown path:



Given

$$\begin{aligned}\Delta S_{(A \rightarrow C)} &= 50 \text{ e.u.} \\ \Delta S_{(C \rightarrow D)} &= 30 \text{ e.u.} \\ \Delta S_{(B \rightarrow D)} &= 20 \text{ e.u.}\end{aligned}$$

where e.u. is entropy unit then  $\Delta S (A \rightarrow B)$  is

- a. +100 e.u.
- b. +60 e.u.
- c. -100 e.u.
- d. -60 e.u.

221. For the process

H<sub>2</sub>O (l) (1 bar, 373 K) → H<sub>2</sub>O (g) (1 bar, 373 K), the correct set of thermodynamic parameters is

- a.  $\Delta G = 0$ ,  $\Delta S = +ve$
- b.  $\Delta G = 0$ ,  $\Delta S = -ve$
- c.  $\Delta G = +ve$ ,  $\Delta S = 0$
- d.  $\Delta G = -ve$ ,  $\Delta S = +ve$

[IIT 2007]

222. The value of  $\log_{10} K$  for a reaction A ⇌ B is (Given:  $\Delta_r H^\circ_{298\text{K}} = -54.07 \text{ kJ mol}^{-1}$ ,  $\Delta_r S^\circ_{298\text{K}} = 10 \text{ JK}^{-1} \text{ mol}^{-1}$  and  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ;  $2.303 \times 8.314 \times 298 = 5705$ )

- a. 10
- b. 100
- c. 5
- d. 95

[IIT 2007]

223. In a constant volume calorimeter, 3.5 of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K<sup>-1</sup>, the numerical value for the enthalpy of combustion of the gas in kJ mol<sup>-1</sup> is

- a. 10
- b. 100
- c. 5
- d. 95

[IIT 2009]

## ANSWERS

### Straight Objective Type Questions

- |       |       |       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1. d  | 2. d  | 3. d  | 4. b  | 5. d  | 6. d  | 7. a  | 8. b  | 9. a  |
| 10. c | 11. d | 12. c | 13. d | 14. a | 15. c | 16. c | 17. c | 18. c |
| 19. d | 20. a | 21. d | 22. d | 23. a | 24. d | 25. a | 26. b | 27. a |
| 28. c | 29. b | 30. a | 31. c | 32. c | 33. a | 34. d | 35. a | 36. b |

## **4.54 ■ Energetics**

37. a	38. a	39. a	40. a	41. b	42. b	43. d	44. b	45. d
46. b	47. d	48. d	49. c	50. b	51. a	52. a	53. b	54. d
55. a	56. b	57. a	58. c	59. a	60. a	61. d	62. b	63. b
64. b	65. d	66. a	67. c	68. b	69. b	70. d	71. d	72. c
73. a	74. c	75. c						

## **Brainteasers Objective Type Questions**

76. a	77. c	78. b	79. a	80. a	81. d	82. a	83. a
84. c	85. b	86. c	87. b	88. a	89. c	90. b	91. c
92. d	93. b	94. b	95. a	96. d	97. a	98. a	99. d
100. a	101. d	102. b	103. b	104. c	105. b	106. b	107. d
108. b	109. d	110. a	111. a	112. a	113. b	114. c	115. d
116. a	117. b	118. d	119. c	120. a	121. d	122. a	123. a
124. b	125. a						

## **Multiple Correct Answer Type Questions**

126. c, d	127. a, c, d	128. a, b, c	129. a, d	130. a, b, d	131. a, c, d
132. a, b, c	133. a, d	134. b, c, d	135. a, b, d	136. a, c	137. a, c
138. b,c,d	139. c, d	140. c, d	141. b, c, d	142. a, d	143. b, c
144. a, b, c	145. a, c	146. a,b,d	147. b,c,d	148. a,c,d	149. a,c,d
150. a, b, d	151. a, b, d	152. a, c, d	153. a, c, d	154. b, c, d	155. a, c, d

## **Linked-Comprehension Type Questions**

### **Comprehension 1**

156. d      157. a      158. c

### **Comprehension 2**

159. b      160. d      161. d

### **Comprehension 3**

162. b      163. c      164. b

### **Comprehension 4**

165. b      166. b      167. d

### **Comprehension 5**

168. b      169. c      170. a

### **Assertion-Reason Type Questions**

171. a	172. b	173. a	174. a
175. b	176. a	177. a	178. a
179. d	180. a	181. a	182. a
183. b	184. d	185. e	186. e
187. c	188. a	189. a	190. a
191. c	192. a	193. a	194. a
195. a			

## Matrix-Match Type Questions

196. A-(q), B-(r), C-(p), D-(s)

198. A-(s), B-(r), C-(q), D-(p)

200. A-(r), B-(s), C-(q), D-(p)

202. A-(q), B-(r), C-(r), D-(p, s)

204. A-(q), B-(p), C-(s), D-(r)

197. A-(q), B-(p, r), C-(s), D-(p, r)

199. A-(s), B-(q), C-(p, s), D-(q, r)

201. A-(q), B-(p), C-(r), D-(q)

203. A-(p), B-(r), C-(r), D-(q)

## The IIT-JEE Corner

205. b

206. d

207. c

208. a

209. b

210. a

211. b

212. a

213. c

214. c

215. b

216. c

217. b

218. c

219. a

220. b

221. a

222. a

223. c

## Hints and Explanations

1. It gives the neutralization of 1 mole  $\text{H}^+$  and 1 mole of  $\text{OH}^-$  ions.

2.  $q = \Delta E - w$  (first law of thermodynamics)

$$q + w = \Delta E$$

Now  $q + w$  is a state function as it is equal to  $\Delta E$  (state function).

3. Equal to  $\Delta H$ .

4. Standard heat of formation of  $\text{C}_2\text{H}_4$  is the heat change when 1 mole of  $\text{C}_2\text{H}_4$  is formed from its elements in the standard state [carbon as graphite and hydrogen as  $\text{H}_2$ ]

6.  $\Delta H_{\text{obs}} = \Delta H + \text{Energy needed to disturb resonance}$

$$= 3 \times -119.5 + 150.4 = -208.1 \text{ kJ mol}^{-1}$$

8.  $\Delta H = \Delta U + \Delta nRT$

(here  $\Delta n$  = number of molecules of products – no. of molecules of reactants)

$$- 92.38 \times 1000 = \Delta U - 2 \times 8.314 \times 298$$

$$\Delta U = - 87424 \text{ J} = - 87.424 \text{ kJ.}$$

9.  $\Delta G^\circ = - RT \ln K$

$[\Delta G^\circ = \text{standard free energy change,}$

$K = \text{equilibrium constant}$

If a substance is in equilibrium between two phases at constant temperature and pressure, its chemical potential must have the same value in both the phases.

So  $\Delta G^\circ = 0$

10. At equilibrium  $\Delta G = 0$ . So  $\Delta H = T\Delta S$

$$\text{So } T = \Delta H / \Delta S = 30 \times 10^{-3} / 105$$

$$= 285.7 \text{ K}$$

11.  $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

For a spontaneous process  $\Delta S_{\text{total}}$  must be positive that is,  $\Delta S_{\text{total}} > 0$

13. At equilibrium  $\Delta G = 0$

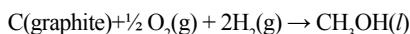
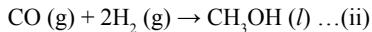
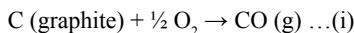
14. Bomb calorimeter is commonly used to find the heat of combustion of organic substances which consists of a sealed combustion chamber, called a bomb. If a process is run in a sealed container then no expansion or compression is allowed,

## 4.56 ■ Energetics

so  $w = 0$  and  $\Delta U = q$ .

$\Delta U < 0$ ,  $w = 0$ .

15. Methanol can be prepared synthetically by heating carbon monoxide and hydrogen gases under pressure in the presence of a catalyst.



16. As  $\Delta n = 0$  so  $\Delta H = \Delta U$

17.  $MgO$  is the oxide of weak base and we know that heat of neutralization of 1 eq. of strong acid with strong base is  $-57.33\text{ kJ/mol}$ .

⇒ With weak base some heat is absorbed in dissociation of weak base.

⇒ Heat of neutralization of weak base with strong acid will be  $-57.33\text{ kJ/mol}$ .

18.  $\Delta G = \Delta H - T\Delta S$

$\Delta G = -ve$  for spontaneous reaction

when  $\Delta S = +ve$ ,  $\Delta H = +ve$

and  $T\Delta S > \Delta H \Rightarrow \Delta G = -ve$

When randomness favours and energy factor do not favour then spontaneity depends upon the temperature dependent means at high temperature.

$T\Delta S > \Delta H$ ,  $\Delta G = -ve$  and reaction is feasible.

19.  $CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3$

$\Delta H = (\text{BE})_{\text{reactants}} - (\text{BE})_{\text{products}}$

$$= 4(\text{BE})_{C-H} + (\text{BE})_{C=C} + (\text{BE})_{H-H}$$

$$- [6(\text{BE})_{C-H} + (\text{BE})_{C-C}]$$

$$= -125\text{ kJ}$$

23. For a spontaneous reaction  $\Delta H = -ve$ ,

$\Delta S = +ve$  spontaneity depends upon both critical minimum energy and maximum randomness/disorder.

24.  $\Delta E = 0$ , in a cyclic process.

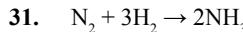
26. Work done due to change in volume against constant pressure is

$$W = -P(V_2 - V_1) = -1 \times 10^5 \text{ Nm}^{-2}$$

$$(1 \times 10^{-2} - 1 \times 10^{-3}) \text{ m}^3$$

$$= -900 \text{ Nm} = -900 \text{ J.}$$

28. From solid state to liquid state entropy increases.



$$\Delta n = 2 - 4 = -2$$

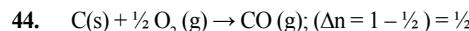
$$\Delta H = \Delta U + \Delta nRT = \Delta U - 2RT$$

$$\Delta H < \Delta U.$$

$$\begin{aligned} 32. \quad W &= -2.303 nRT \log \frac{V_2}{V_1} \\ &= -2.303 \times 1 \times 2 \times 300 \times \log \frac{10}{1} \\ &= -1381.8 \text{ cal.} \end{aligned}$$

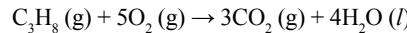
37. Work done is reversible process is maximum. Thus  $T_2 \ll T_1$  in reversible process or  $T_{2\text{rev}} \ll T_2 \text{ irr.}$

42.  $\Delta H = \Delta E + \Delta n g RT$   
as  $\Delta n g = np - nr = 8 - 8 = 0$ ,  
thus  $\Delta H = \Delta E$ .



$$\begin{aligned} \Delta H - \Delta U &= \Delta nRT = + \frac{1}{2} \times 8.314 \times 298 \\ &= + 1238.78 \text{ J mol}^{-1} \end{aligned}$$

45. For the reaction



$$\Delta n = n_p - n_r$$

$$= 3 - 6 = -3$$

$$\Delta H = \Delta E + \Delta nRT$$

$$\Delta H - \Delta E = \Delta nRT = -3RT$$

$$\begin{aligned} 46. \quad \Delta S &= \frac{\Delta H_f}{T} = \frac{6.0}{273} = 0.02198 \text{ kJ K}^{-1} \text{ mol}^{-1} \\ &= 0.02198 \times 1000 \text{ JK}^{-1} \text{ mol}^{-1} \\ &= 21.98 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$48. \quad C = \frac{q}{m(T_2 - T_1)}.$$

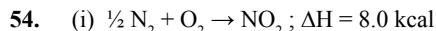
$$75 = \frac{1000}{5.55(\Delta T)} \quad (m = 100/8 = 5.55)$$

$$\Delta T = \frac{1000}{5.55 \times 75} = 2.4 \text{ K}$$

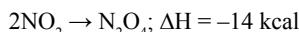
50. In irreversible process

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

so in the spontaneous process  $\Delta S$  is positive



Multiply (i) by 2 subtract from (ii), we get



55.  $W = -2.303 nRT \log \frac{P_1}{P_2}$

$$= -2.303 \times 1 \times 2 \times 300 \log \frac{1}{1}$$

$$= -1381.8 \approx -1382 \text{ cal}$$

56. Weakest acid has the lowest heat of neutralization because more heat is absorbed in the ionization of weak acid

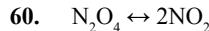
57. A salt which absorbs more heat for dissolution in water give maximum cooling.

58.  $T(\text{m.p.}) = 27 + 273 = 300 \text{ K}$

$$\Delta H_{\text{fus.}} = 600 \text{ cal/mole}$$

$$\Delta S = \frac{\Delta H}{T} = \frac{600}{300} = 2$$

59. On set of crystallization in a super cooled liquid is called Devitrification. The process of crystallization leads to decrease in entropy.



On heating, since the colour depends that is more of  $\text{NO}_2$  is formed and the forward reaction is favoured. Thus, the forward reaction is endothermic that is,  $\Delta H = +ve$

62. Heat of combustion is always negative.

63.  $\Delta H_f^\circ$  of graphite is taken as zero. For diamond, its value is  $1.9 \text{ kJ mol}^{-1}$  that is, greater than graphite.

64. The molar heat capacity is the heat required to raise the temperature of one mole of the gas by  $1^\circ\text{C}$ .

$$C_v = \frac{3}{2} R$$

40 gram of argon means 1 mole.

Here  $C_v = 3 \text{ cal}$

Thus the heat required to raise the temperature by  $60^\circ\text{C}$  is  $60 \times 3 = 180 \text{ cal}$ .

66. Smallest = eV and largest = lit atm

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J,}$$

$$1 \text{ cal} = 4.186 \text{ J,}$$

$1 \text{ erg} = 10^{-7} \text{ J}$

$1 \text{ lit atm} = 101.3 \text{ J}$

67. As  $\Delta G^\circ = -RT \ln K$ .

When  $K < 1.0, \Delta G^\circ = +ve$

68. State functions or state variables depend only on the state of the system. Here 'w' represents work done and 'q' represents amount of heat so both of these are not state functions.

69. For this process  $\frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{Cl}^-(\text{aq})$

$$\Delta H = \frac{1}{2} \Delta H_{\text{diss}} \text{ of } \text{Cl}_2 + \Delta_{\text{eq}} \text{ Cl} + \Delta_{\text{hyd}} \text{ Cl}^-$$

$$= + \frac{240}{2} - 349 - 381$$

70.  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

$$\Delta H = \Delta E + \Delta nRT$$

Here,  $\Delta n$  = Change in number of moles of product and reactant

As  $\Delta n$  + ve, so  $\Delta H = +ve$

$$\Delta S = S_{\text{Product}} - S_{\text{Reactant}}$$

$$\Delta S = +ve$$

71.  $\text{S}(\text{rh}) + 3/2\text{O}_{2(\text{g})} \rightarrow \text{SO}_{3(\text{g})}, \Delta H_1 = 2x \text{ kJ mol}^{-1} \text{ (i)}$

- $\text{SO}_{2(\text{g})} + 1/2\text{O}_{2(\text{g})} \rightarrow \text{SO}_{3(\text{g})}, \Delta H_2 = -y \text{ J mol}^{-1} \text{ (ii)}$

From equation (i) – (ii) we have

$$\text{S}_{(\text{rh})} + \text{O}_{2(\text{g})} \rightarrow \text{SO}_{2(\text{g})}, \Delta H_r = \Delta H_1 - \Delta H_2 = -2x + y$$

Here of formation of  $\text{SO}_2$  ( $\Delta H_r$ ) =  $y - 2x$

72. Al acts as a good reducing agent and reduces oxides of metals like Cr, Fe, Mn, etc.



Therefore  $\Delta G^\circ$  for the formation of  $\text{Al}_2\text{O}_3$  is lower in comparison to  $\Delta G^\circ$  for the formation of  $\text{Cr}_2\text{O}_3$ .

73.  $\text{NH}_{3(\text{g})} + \text{HCl}_{(\text{g})} \rightarrow \text{NH}_4\text{Cl}_{(\text{g})}$

$\Delta n$  = no. of moles of product – no. of moles of reactant

$$= 1 - 2$$

$$\Delta n = -1$$

Now,  $\Delta H = \Delta E + \Delta nRT$

$$\Delta H = \Delta E - RT \text{ or } \Delta E = \Delta H + RT$$

As,  $\Delta E > \Delta H$  ( $\Delta E - \Delta U$ ) = change in internal energy.

## 4.58 ■ Energetics

75. It can be derived as

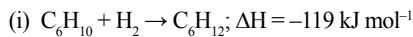
$$[\partial(\Delta G/T)/\partial T]_p = -\Delta H/T^2$$

$$\Delta H = -T^2 [\partial(G/T)/\partial T]_p$$

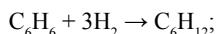
It is a form of Gibbs-Helmholtz equation.

### Brainteasers Objective Type Questions

76. Given



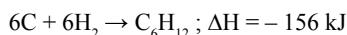
This reaction involves breaking up of one double bond and addition of one  $\text{H}_2$  molecule.



$$\Delta H = 3 \times -119 = -357 \text{ kJ}$$

(because, this reaction involves breaking up of one double bond and addition of three  $\text{H}_2$  molecules).

Also given



Thus, resonance energy = difference between  $\Delta H_f$  (obs) –  $\Delta H_f$  (calc) = 49 – 201 = –152 kJ

77. (c) For the temperature of the solution decrease the solvent water must lose energy. The process of ammonium and nitrate ions in solid ammonium nitrate dissolving and becoming hydrated must therefore absorb energy from water.

79.  $\Delta H - \Delta E = \Delta n g RT$

$$= (12 - 15) \times \frac{8.314}{1000} \times 298$$

$$= -7.433 \text{ kJ mol}^{-1}$$

80. Amount of HCl added =  $\frac{100 \times 0.3}{1000}$

$$= 0.03 \text{ mol}$$

$$\text{Amount of NaOH added} = \frac{100 \times 0.33}{1000}$$

$$= 0.033 \text{ mol}$$

limiting reagent = 0.03 mol of HCl

So amount of heat evolved =  $57.1 \times 0.03$

$$= 1.713 \text{ kJ}$$

81. Amount of energy left unused

$$= \frac{1560}{2} = 780 \text{ kJ}$$

Amount of water perspired

$$= \frac{\text{Energy left unused}}{\text{Enthalpy of evaporation of water}}$$

$$= \frac{780 \text{ kJ}}{44 \text{ kJ mol}^{-1}} = \frac{780}{44} \text{ mole}$$

$$= \frac{780 \times 18}{44} = 319.14 \text{ g}$$

82.  $\Delta H_{\text{CO}_2}/\Delta H_{\text{CO}} = 2.56$

$$\Delta H_{\text{CO}_2} = 2.56 \Delta H_{\text{CO}}$$

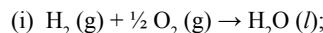
$$177.5 = \Delta H_{\text{CO}} - \Delta H_{\text{CO}_2}$$

$$= \Delta H_{\text{CO}} - 2.56 \Delta H_{\text{CO}}$$

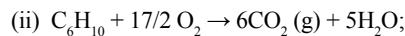
$$\Delta H_{\text{CO}} = -\frac{177.5}{1.56} = -113.78 \text{ kJ mol}^{-1}$$

83. For dissolution of gases in water,  $\Delta S = -ve$  (non-favorable factor). Since this process is spontaneous ( $\Delta G = -ve$ ) so  $\Delta H$  has to be –ve (favorable factor) and the process is exothermic.

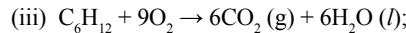
84. Given that



$$\Delta H = -241 \text{ kJ}$$

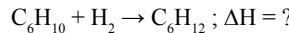


$$\Delta H = -3800 \text{ kJ}$$



$$\Delta H = -3920 \text{ kJ}$$

Our aim is to get



So Add (i) and (ii) and then subtract (iii), to get

$$\Delta H = -121 \text{ kJ mol}^{-1}$$

86.  $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

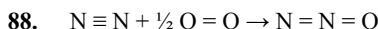
$$= [\Delta H_f(\text{CO}_2) + 2 \Delta H_f(\text{H}_2\text{O})] - [\Delta H_f(\text{CH}_4) + 2 \Delta H_f(\text{CO}_2)] \\ = [-394.8 + 2 \times -241.6] - [-76.2 + 0]$$

$$= -878.0 + 76.2 = 802.2 \text{ kJ mol}^{-1}$$

now  $22.4 \text{ L}$  (or  $22.4 \times 10^{-3} \text{ m}^3$ ) of  $\text{CH}_4$  on combustion give heat =  $802.2 \text{ kJ mol}^{-1}$

$$1 \text{ m}^3 = \frac{802.2}{22.4 \times 10^{-3}}.$$

$$= 35812 \text{ kJ mol}^{-1}$$



$$\Delta H_f^\circ = \sum \text{BE of reactants} - \sum \text{BE of products}$$

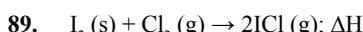
$$= [\text{BE}(\text{N}\equiv\text{N}) + \frac{1}{2} \text{ BE}(\text{O}=\text{O})] - [\text{BE}(\text{N}=\text{N}) + \text{BE}(\text{N}=\text{O})]$$

$$= (946 + \frac{1}{2} \times 498) - (418 + 607) = 170 \text{ kJ}$$

resonance energy

$$= \Delta H_f^\circ (\text{observed}) - \Delta H_f^\circ (\text{calculated})$$

$$= 82 - 170 = -88 \text{ kJ mol}^{-1}$$

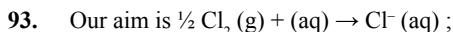


$$\Delta H = [\varepsilon\text{Cl}_2 + \varepsilon 2(\text{s}) \rightarrow (\text{g}) + \varepsilon\text{I}_2(\text{g})] - 2 \times [\varepsilon\text{ICl}]$$

$$= [242.3 + 62.76 + 151.0] - 2 \times [211.3]$$

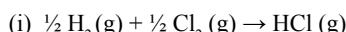
$$= 33.46$$

$$\Delta H_f^\circ = \frac{33.46}{2} = 16.83 \text{ kJ mol}^{-1}$$

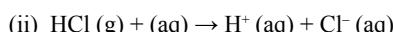


$$\Delta H = ?$$

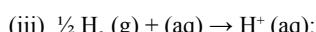
Given is



$$\Delta H = -92.4 \text{ kJ}$$



$$\Delta H = -74.8 \text{ kJ}$$



$$\Delta H = 0.0 \text{ kJ}$$

Operate (i) + (ii) - (iii), we obtain

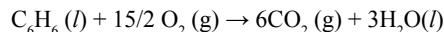
$$\Delta H_f^\circ \text{ of } \text{Cl}^-(\text{aq}) = -167.2 \text{ kJ}$$

0.16 g of methane is subjected to combustion at  $27^\circ\text{C}$  in a bomb calorimeter system. The temperature of the calorimeter system (including water) was found to rise by  $0.5^\circ\text{C}$ .

95.  $\Delta E \text{ per mole} = \frac{327}{7.8} \times 78 = -3270 \text{ kJ}$

$$T = 27 + 273 = 300 \text{ K},$$

$$R = 8.3/1000 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

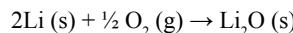


$$\Delta n_g = n_p - n_r = 6 - 15/2 = -3/2$$

$$\Delta H = \Delta E + \Delta n_g RT$$

$$\Delta H = -3270 + [(-3/2) \times (8.3/1000) \times 300]$$

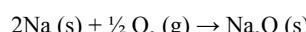
$$\Delta H = -3274 \text{ kJ}$$



$$\Delta G_f^\circ(\text{Li}_2\text{O}) = \Delta H_f^\circ - T\Delta S^\circ$$

$$= 1244 - (298 \times 6) = -544 \text{ kJ mol}^{-1}$$

For  $\text{Na}_2\text{O}$ ,



$$\Delta G_f^\circ(\text{Na}_2\text{O}) = \Delta H_f^\circ - T\Delta S^\circ$$

$$= 1411 - (298 \times 6) = -377 \text{ kJ mol}^{-1}$$

For reaction,



$$\Delta G^\circ = 3 \times \Delta G_f^\circ(\text{Na}_2\text{O}) - \Delta G_f^\circ(\text{Al}_2\text{O}_3)$$

$$= 3 \times (-377) - (-1582) = +451 \text{ kJ mol}^{-1}$$

Similarly when Li is used, then

$$\Delta G^\circ = 3 \times \Delta G_f^\circ(\text{Li}_2\text{O}) - \Delta G_f^\circ(\text{Al}_2\text{O}_3)$$

$$= 3 \times (-544) - (-1582)$$

$$= -1632 + 1582 = -50 \text{ kJ mol}^{-1}$$

As  $\Delta G^\circ$  is negative when Li is used for the reduction, so the reaction is feasible.

99.  $\Delta n_g = n_p - n_r = 5 - 3 = 2$

$$\Delta H = \Delta E + \Delta n_g RT$$

$$\Delta E = \Delta H - \Delta n_g RT$$

$$= 19 - (2 \times 2 \times 10^{-3} \times 300)$$

$$= 19 - 1.2 = 17.8 \text{ kcal}$$

## 4.60 ■ Energetics

100.  $\Delta H = m \times T_b$

$$= 90 \times 540 = 48600 \text{ cal}$$

$$\Delta H = \Delta E + P\Delta V$$

$$\Delta H = \Delta E + P(V_g - V_l)$$

since the volume of liquid is negligible as compared to volume of its vapour, so

$$V_g \gg V_l$$

$$\Delta H = \Delta E + P.V_g$$

$$\Delta H = \Delta E + nRT \quad (PV = nRT)$$

$$\Delta E = \Delta H - nRT$$

$$= 48600 - (90/18 \times 2 \times 373)$$

$$= 44870 \text{ cal.}$$

101.  $W = P(V_2 - V_1)$

$$= nRT_2 - nRT_1$$

$$T_2 - T_1 = \frac{W}{nR}.$$

$$Q = n C_p (T_2 - T_1)$$

$$506 = n C_p \frac{W}{nR}.$$

$$506 = \frac{C_p W}{R}$$

$$C_p = \frac{506 R}{144.5} = 7/2 R$$

So gas is diatomic  $O_2$ .

103.  $\Delta G^\circ = -2.303 RT \log K$

$$-4.606 = -2.303 \times \frac{2}{100} \times 500 \log K$$

$$\log K = \frac{-4.606}{-2.303 \times 2/100 \times 500} = 2$$

$$K = \text{antilog } (2) = 100$$



Energy is supplied to the system for complete the reaction that is, energy of the reactant side is less than the product side.

108. Here, option c is not correct as

$Z \rightarrow x$  is isochoric process

$V \rightarrow \text{constant}$

i.e.,  $P \propto T$

$$P_x > P_z$$

$T_x > T_z$  or  $\Delta UZ \times$  is positive and not negative.

109. (i)

$$W_{\text{rev}, \text{isothermal}} = n \times 2.303 RT \log \frac{P_1}{P_2}$$

$$= 2 \text{ mol} \times 2.303 \times 2 \text{ cal K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times 1$$

$$= 2764 \text{ cal}$$

(ii) Work of expansion =  $P \cdot \Delta V$

$$= 1 \text{ atm} \times 0.08212 \text{ lit}$$

$$= 0.08212 \text{ lit-atm} = 2 \text{ cal}$$

110. For reversible adiabatic change,

$$T \cdot V^{\gamma-1} = \text{constant}$$

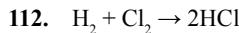
$$\frac{T_2}{T_1} = \frac{V_1^{\gamma-1}}{V_2^{\gamma-1}} = (1/10)^{\gamma-1} = (1/10)^{0.666}$$

Since  $\gamma$  for a monobasic gas =  $5/3 = 1.666$ .

111. As C (graphite)  $\rightarrow$  C (gas)

$$\Delta H = 725 \text{ kJ/mol}$$

As graphite is thermodynamically more stable than diamond therefore the heat required to convert graphite to gaseous carbon should be more.



$$\Delta H_{\text{reaction}} = \Sigma(\text{B.E})_{\text{reactant}} - \Sigma(\text{B.E})_{\text{product}}$$

$$= [(B.E)H - H + (B.E)Cl - Cl] - [2(B.E)H - Cl]$$

$$= 434 + 242 - (431) \times 2$$

$$= -186 \text{ kJ}$$

$$\text{As } \Delta H_{\text{reaction}} = -186 \text{ kJ}$$

So, enthalpy of formation of HCl

$$= \frac{-186}{2} \text{ kJ} = -93 \text{ kJ mol}^{-1}$$

115. (i)

$$W_{\text{rev}, \text{isothermal}} = n \times 2.303 RT \log \frac{P_1}{P_2}$$

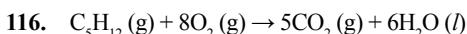
$$= 2 \text{ mol} \times 2.303 \times 2 \text{ cal K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times 1$$

$$= 2764 \text{ cal}$$

$$(ii) \text{ Work of expansion} = P \cdot \Delta V$$

$$= 1 \text{ atm} \times 0.08212 \text{ lit}$$

$$= 0.08212 \text{ lit-atm} = 2 \text{ cal}$$

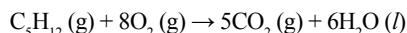


$$\Delta G^\circ = [(-394.4 \times 5) + (-237.2 \times 6)] - [(-8.2) + (8 \times 0)]$$

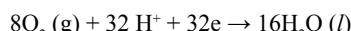
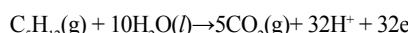
$$= -3387.5 \text{ kJ.}$$

The standard free energy change of elementary substances is taken as zero.

For the fuel cell, the complete cell reaction is:



This reaction is the combination of the following two half reactions:



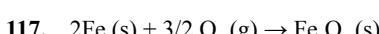
As the number of electrons exchanged is 32 here, so  $n = 32$

$$\Delta G^\circ = -nFE^\circ$$

$$-3387.5 \times 10^3 \text{ J} = -32 \times 96500 \text{ J/Volt} \times E^\circ$$

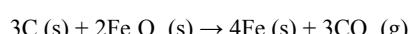
On solving, we get

$$E^\circ = 1.09698 \text{ V.}$$

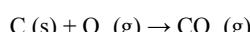


$$\Delta H^\circ = ?$$

Given

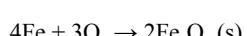


$$\Delta H^\circ = -93657 \text{ kcal} \dots (1)$$



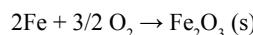
$$\Delta H^\circ = -94050 \text{ kcal} \dots (2)$$

On subtracting equation (1) from (2), we get



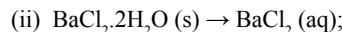
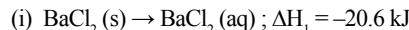
$$\Delta H^\circ = -393 \text{ kcal}$$

So



$$\Delta H^\circ = -196.5 \text{ kcal at } 25^\circ\text{C}$$

**118.** Given

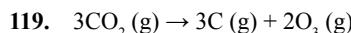


$$\Delta H_2 = 8.8 \text{ kJ}$$

now subtract (ii) from (i), we obtain



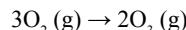
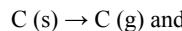
$$\Delta H = \Delta H_1 - \Delta H_2 = -29.4 \text{ kJ}$$



$$\Delta H = 3\Delta H_{\text{atomisation}} [\text{C}(\text{s}) \rightarrow \text{C}(\text{g})] + 2\Delta H_f^\circ [\text{O}_3(\text{g})] \\ - 3\Delta H_f^\circ [\text{CO}_2(\text{g})]$$

$$\Delta H = 3\Delta H_{\text{atomisation}} [\text{C}(\text{s}) \rightarrow \text{C}(\text{g})] + 2\Delta H_f^\circ [\text{O}_3(\text{g})] \\ - 3 \times 409$$

As energy will be required for the processes



So  $\Delta H$  will be more than 1227 kJ.

**120.**  $n = 1, P_1 = 1 \text{ bar},$

$$P_2 = 0.1 \text{ bar}, T = 273 \text{ K}$$

$$W = -2.303 nRT \log P_1/P_2$$

$$= -2.303 \times 1 \times 8.314 \times 273 \log 1/0.1$$

$$= -2.303 \times 1 \times 8.314 \times 273 \times 1$$

$$= -5227 \text{ J}$$

$$= -5.227 \text{ kJ}$$

now,  $q = \Delta E - w$

since temperature is constant,  $\Delta E = 0$

$$q = -w = + 5.227 \text{ kJ}$$

**121.** Heat produced by the combustion of 0.16 g of  $\text{CH}_4$   $= 17.7 \times 0.5 = 8.85 \text{ kJ}$

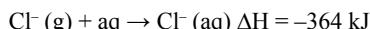
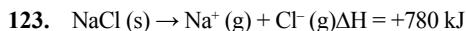
Heat produced by the combustion of 1.0 mole of

$$\text{CH}_4(16 \text{ g}) = \frac{8.85 \times 16}{0.16} = 885 \text{ kJ}$$

## 4.62 ■ Energetics

As combustion has been carried in bomb, calorimeter (closed vessel), the heat produced is  $q_v$  that is,

$$q_v = -885 \text{ kJ}$$



The net reaction is dissolution of  $\text{NaCl}(\text{s})$ .  $\Delta H_{\text{solution}} = 780 - (406 + 364) = 10 \text{ kJ mol}^{-1}$

### Multiple Correct Answer Type Questions

150. Entropy of gas is greater than that of liquid and solid. In option (c) solid is converted to gaseous phase.

Entropy of gas > liquid > solid.

### Linked-Comprehension Type Questions

161. To be spontaneous,  $\Delta G$  must be negative ( $\Delta G < 0$ )

Thus,  $\Delta H^\circ - T\Delta S^\circ < 0$ ;

$$\Delta H < T\Delta S^\circ ;$$

$$T > \Delta H^\circ / \Delta S^\circ$$

$$T > \frac{572 \text{ kJ}}{0.179 \text{ kJ} / \text{K}}$$

$$= 3200 \text{ K}$$

### The IIT-JEE Corner

206.  $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$

The standard molar enthalpy of formation of  $\text{CO}_2$  is equal to the standard molar enthalpy of combustion of carbon (graphite).

207. As energy available for muscular work

$$= \frac{2880 \times 25}{100} = 720 \text{ kJ mol}^{-1}$$

so energy available for muscular work for 120 g of

$$\text{glucose} = 720 \times \frac{120}{180} = 480 \text{ kJ}$$

as 100 kJ is used for walking = 1 km

so 480 kJ is used for walking

$$= 1 \times \frac{480}{100} = 4.8 \text{ km}$$

208. If  $\text{AlCl}_3$  is present in ionic state in aqueous solution ( $\text{Al}^{3+}$  and three  $\text{Cl}^-$  ions), then standard heat of hydration of  $\text{Al}^{3+}$  and three  $\text{Cl}^-$  ions.

$$\begin{aligned} \Delta H^\circ(\text{hydration}) &= -4665 + (3 \times -381) \\ &= -5808 \text{ kJ mol}^{-1}. \end{aligned}$$

As hydration energy is greater than ionization energy of Al, so  $\text{AlCl}_3$  would be ionic in solution.

210. Combustion is always exothermic.

$$\Delta H = -\text{ve}$$

211.  $\Delta H = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$

$$\begin{aligned} &= [\Delta H_f^\circ(\text{CO}) + \Delta H_f^\circ(\text{H}_2\text{O})] - [\Delta H_f^\circ(\text{CO}_2) \\ &\quad + \Delta H_f^\circ(\text{H}_2)] \\ &= [-110.5 - 241.8] - [-393.5 + 0] \\ &= -352.3 + 393.5 = +41.2 \text{ kJ} \end{aligned}$$

212. Statement A is false, as work is a path function. The driving force and the opposing force differ by infinitesimal small amount. So, the system and surroundings always remain in equilibrium state with one another

214.  $\Delta H = \Delta U + \Delta(PV)$

$$\begin{aligned} &= \Delta U + (P_2 V_2 - P_1 V_1) \\ &= 30 + (4 \times 5 - 2 \times 3) \\ &= 30 + 14 = 44 \text{ atm} \end{aligned}$$

216. As  $\Delta H = nC_p \Delta T$

As for isothermal process,  $\Delta T = 0$ ,

hence  $\Delta H = 0$

217. As  $\Delta S = \frac{\Delta Q_{\text{rev}}}{T}$

$$\text{So } T = \frac{\Delta Q}{\Delta S} = 30 \times \frac{1000}{75} = 400 \text{ K}$$

218. During adiabatic irreversible process,  $W_{\text{surr.}} = \Delta E = -P\Delta V$ ,  $nC_V \Delta T = -P\Delta V$

$$1 \times \frac{R}{\gamma - 1} \times (T_f - T_i) = -P(V_2 - V_1)$$

$$T_f = T_i - \frac{(\gamma - 1)}{R} P(V_2 - V_1)$$

$$T_f = T_i - \frac{T(5/3 - 1) \times 1 \times (2 - 1)}{0.0821}$$

$$T_f = T_i - \frac{2}{3 \times 0.0821}.$$

- $$219. \quad \Delta H = \Delta U + \Delta(PV)$$

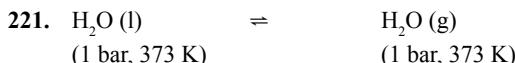
$$\Delta H = \Delta U + V \Delta P$$

$$\Delta U = \Delta H - V\Delta P = -560 + 1 \times 30 \times 0.1$$

$$= -557$$

absolute value = 557 kJ

- $$\Delta S(A \rightarrow B) = \Delta S(A \rightarrow C) + \Delta S(C \rightarrow D) - \Delta S(B \rightarrow D) \\ = 50 + 30 - 20 = 60 \text{ e.u.}$$



At 100°C, H<sub>2</sub>O (*l*) has equilibrium with H<sub>2</sub>O (*g*) therefore ΔG = 0.

As liquid molecules are converting into gases molecules therefore  $\Delta S$  = positive.

- $$222. \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -54.07 \times 1000 - 298 \times 10$$

$$= -57050 \text{ J mol}^{-1}$$

$$-57050 = -5705 \log_{10} K$$

$$\log_{10} K = 10$$

## Numericals For Practice

1. Calculate the heat evolved when 0.500 g of  $\text{Cl}_2(\text{g})$  reacts with an excess of  $\text{HBr}(\text{g})$  to form  $\text{HCl}(\text{g})$  and  $\text{Br}_2(\text{l})$ , given the following standard enthalpies of formation (kJ/mol):  $\text{HCl}(\text{g}), -92.30;$   $\text{HBr}(-36.20)$

- a.** 0.791      **b.** 7.91  
**c.** 79.1      **d.** 791.0

- $2\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{N}_2\text{O}(\text{g})$ , at 298 K,  $\Delta H$  is 164 kJ mol<sup>-1</sup>. The  $\Delta E$  of the reaction is

- a.  $269 \text{ kJ mol}^{-1}$
  - b.  $166.5 \text{ kJ mol}^{-1}$
  - c.  $144.05 \text{ kJ mol}^{-1}$
  - d.  $151.8 \text{ kJ mol}^{-1}$

3. The temperature above which a reaction would become spontaneous, if  $\Delta H$  and  $\Delta S$  of the reaction, at this temperature, are respectively 90 kJ and  $90 \text{ J K}^{-1}$  is

- a.**  $0^{\circ}\text{C}$       **b.**  $1000^{\circ}\text{C}$   
**c.**  $2000\text{ K}$       **d.**  $1000\text{ K}$

4. The enthalpies of combustion of carbon and carbon monoxide are  $-393.5$  and  $-283 \text{ kJ mol}^{-1}$  respectively. The enthalpy of formation of carbon monoxide per mole is

- a.**  $-676.5 \text{ kJ}$       **b.**  $-110.5 \text{ kJ}$   
**c.**  $110.5 \text{ kJ}$       **d.**  $676.5 \text{ kJ}$

5. Given that  $\Delta H^\circ = -311 \text{ kJ}$  for the hydrogenation of



and the following bond dissociation energies, estimate a value for the C – to –C triple bond dissociation energy.

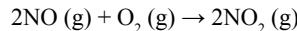
Bond	D, kJ/mol
C – C	350
C – H	410
H – H	436

- a. 1807 kJ/mol
  - b. 807 kJ/mol
  - c. 8017 kJ/mol
  - d. 708 kJ/mol

6. The enthalpy of combustion of methane is  $-880 \text{ kJ}$ . The volume of the methane at STP to be burnt to produce  $2640 \text{ kJ}$  of heat is

- a.** 67.2 L      **b.** 89.8 L  
**c.** 22.4 L      **d.** 11.2 L

7. Calculate the standard free energy change at 25°C for the reaction



Species	$\Delta H_f^\circ$ kJ/mol	$S^\circ$ , J K $^{-1}$ mol $^{-1}$
NO (g)	90.25	210.8
O $_2$ (g)	0.00	205.1
NO $_2$ (g)	33.18	240.1

## 4.64 ■ Energetics

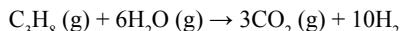
8. The molar entropy of vapourization of acetic acid is 14.5 cal K<sup>-1</sup> mol<sup>-1</sup> at its boiling point 117°C. The latent heat of vapourization of acetic acid is

- a. 84 cal g<sup>-1</sup>      b. 94.25 cal g<sup>-1</sup>  
c. 64 cal g<sup>-1</sup>      d. 47.25 cal g<sup>-1</sup>

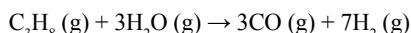
9. A gas absorbs 120 J of heat and expands against the external pressure of 1.5 atm from a volume of 0.5 L to 1 L. The change in internal energy is

- a. 54.02 J      b. 4.42 J  
c. 44.02 J      d. -44.02 J

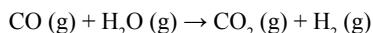
10. Find ΔH for:



Given:



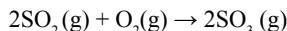
$$\Delta H = 499 \text{ kJ}$$



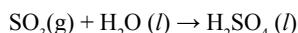
$$\Delta H = -41 \text{ kJ}$$

- a. 316 kJ      b. 476 kJ  
c. 296 kJ      d. 376 kJ

11. Given the following data:

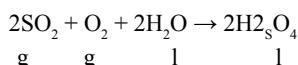


$$\Delta H = -196.7 \text{ kJ/mol}$$



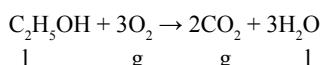
$$\Delta H = -130.1 \text{ kJ/mol}$$

What is the enthalpy of reaction for



- a. -456.9 kJ      b. 326.7 kJ  
c. 456.9 kJ      d. -326.7 kJ

12. Given the following:

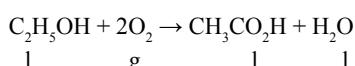


$$\Delta H = -1366.9 \text{ kJ}$$



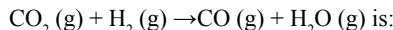
$$\Delta H = -869.9 \text{ kJ}$$

What is the enthalpy of reaction for



- a. 497.0 kJ      b. 2237 kJ  
c. -497.0 kJ      d. -2237 kJ

13. The Δ<sub>f</sub>H° for CO<sub>2</sub>(g), CO(g) and H<sub>2</sub>O(g) are—393.5, -110.5 and -241.8 kJ mol<sup>-1</sup> respectively. The standard enthalpy change (in kJ) for the reaction

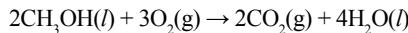


- a. -41.4      b. -14.2  
c. -241.4      d. +41.2

14. At 300 K, the standard enthalpies of formation of C<sub>6</sub>H<sub>5</sub>COOH(s), CO<sub>2</sub>(g) and H<sub>2</sub>O(s) are -408, -393 and -286 kJ mol<sup>-1</sup> respectively. Calculate the heat of combustion of benzoic acid at constant volume.

- a. -3296 kJ mol<sup>-1</sup>      b. -3200 kJ mol<sup>-1</sup>  
c. -3201 kJ mol<sup>-1</sup>      d. -3603 kJ mol<sup>-1</sup>

15. Calculate the standard free energy for the reaction given



Species	ΔG <sub>f</sub> ° kJ mol <sup>-1</sup>
CH <sub>3</sub> OH(l)	-166.3
O <sub>2</sub> (g)	0.00
CO <sub>2</sub> (g)	-394.4
H <sub>2</sub> O(l)	-237.1

- a. -1404.6 kJ      b. -404.6 kJ  
c. -2404.6 kJ      d. 1804.8 kJ

16. Heats of solution of BaCl<sub>2</sub>(s) and BaCl<sub>2</sub>.2H<sub>2</sub>O(s) are -22.8 kJ mol<sup>-1</sup> and 10.8 kJ mol<sup>-1</sup> respectively. ΔH hydration of BaCl<sub>2</sub> to BaCl<sub>2</sub>.2H<sub>2</sub>O is

- a. 33.6 kJ      b. -33.6 kJ  
c. 12.0 kJ      d. -12.0 kJ

17. The molal freezing point constant of naphthalene is 6.9 K mol<sup>-1</sup>. The enthalpy of fusion of solid naphthalene is 4.635 k cal mol<sup>-1</sup>. The melting point of solid naphthalene is

- a. 40.6°C      b. 75.7°C  
c. 80.45°C      d. 82.0°C

18. The bond energies of C=C and C-C at 298 K are 592 and 333 kJ mol<sup>-1</sup> respectively. The enthalpy of polymerization per mole of ethylene is

- a. -66 kJ      b. 76 kJ  
c. -76 kJ      d. -75 kJ

19. If the bond dissociation energies of XY, X<sub>2</sub> and Y<sub>2</sub> are in the ratio of 1 : 1 : 0.5 and ΔH<sub>f</sub> for the formation of XY is -200 kJ/mole. The bond dissociation energy of X<sub>2</sub> will be?

- a.** 100 kJ/mole      **b.** 400 kJ/mole  
**c.** 600 kJ/mole      **d.** 800 kJ/mole
- 20.** The maximum work done in expanding 16 g oxygen at 300 K and occupying a volume of  $7 \text{ dm}^3$  isothermally until the volume becomes  $35 \text{ dm}^3$  is:  
**a.**  $+2.02 \times 10^3 \text{ J}$       **b.**  $-1.30 \times 10^3 \text{ J}$   
**c.**  $-2.01 \times 10^3 \text{ J}$       **d.**  $-12.11 \times 10^3 \text{ J}$
- 21.** Use the given standard enthalpies of formation to calculate  $\Delta H^\circ$  for the following reaction:
- $$3\text{Fe}_2\text{O}_3(\text{s}) + \text{CO}(\text{g}) \rightarrow 2\text{Fe}_3\text{O}_4(\text{s}) + \text{CO}_2(\text{g})$$
- | Species                           | $\Delta H_{f^\circ}^\circ \text{ kJ/mol}$ |
|-----------------------------------|-------------------------------------------|
| $\text{Fe}_2\text{O}_3(\text{s})$ | -824.2                                    |
| $\text{Fe}_3\text{O}_4(\text{s})$ | -1118.4                                   |
| $\text{CO}(\text{g})$             | -110.5                                    |
| $\text{CO}_2(\text{g})$           | -393.5                                    |
- a.** +47.2 kJ      **b.** -477.2 kJ  
**c.** -417.2 kJ      **d.** -47.2 kJ
- 22.** Standard enthalpy and standard entropy changes for the oxidation of ammonia at 298 K are  $-382.64 \text{ kJ mol}^{-1}$  and  $-145.6 \text{ JK}^{-1} \text{ mol}^{-1}$ , respectively. Standard Gibbs energy change for the same reaction at 268 K is  
**a.**  $-221.1 \text{ kJ mol}^{-1}$   
**b.**  $-339.3 \text{ kJ mol}^{-1}$   
**c.**  $-439.3 \text{ kJ mol}^{-1}$   
**d.**  $-523.2 \text{ kJ mol}^{-1}$
- 23.** The enthalpies of formation of  $\text{N}_2\text{O}$  and NO are 30 and 90 kJ  $\text{mol}^{-1}$  respectively. The enthalpy of the reaction,
- $$2\text{N}_2\text{O}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g})$$
- is equal to  
**a.** 300 kJ      **b.** -360 kJ  
**c.** 360 kJ      **d.** -300 kJ
- 24.** Calculate the work done when 50 g of iron reacts with HCl in an open beaker at 25°C.  
**a.** -221.32 J      **b.** -2212.2 J  
**c.** -22.122 J      **d.** none
- 25.** Using bond energy data, calculate heat of formation of isoprene. Given B.E. of C – H = 98.8 kcal, H – H = 104 kcal, C – C = 83 kcal, C = C = 147 kcal and C(s)  $\rightarrow$  C(g) = 171 kcal.  
**a.** 28.3 kcal      **b.** 20.3 kcal  
**c.** 283 kcal      **d.** 206 kcal
- 26.** For the reaction  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ ,  $\Delta H = -85.4 \text{ kJ}$  and  $\Delta S = -188.3 \text{ JK}^{-1}$ . The temperature at which  $\Delta G$  will be zero is

- a.** 0 K      **b.** 548 K  
**c.** 253 K      **d.** 453.53 K
- 27.** Calculate  $\Delta S_f^\circ$  at 25°C for  $\text{PCl}_5(\text{g})$ . Given  $\Delta H_f^\circ = -374.9 \text{ kJ/mol}$  and  $\Delta G_f^\circ = -305 \text{ kJ/mol}$   
**a.** -235 J/mole K  
**b.** -23.5 J/mole K  
**c.** -2.35 J/mole K  
**d.** None
- 28.** Given enthalpy of combustion of glucose is 2870 kJ/mol. What will be the amount of glucose a man has to eat in order to climb a height of 100 m assuming 100% efficiency of the body system (weight of man = 60 kg)  
**a.** 37 g      **b.** 3.7 g  
**c.** 370 g      **d.** 180 g
- 29.** The enthalpy change accompanying the formation of 1 mole  $\text{NH}_3(\text{g})$  from its elements at 298 K is -56.1 kJ. The internal energy is  
**a.** 44.6 kJ      **b.** -53.6 kJ  
**c.** -34.6 kJ      **d.** 53.6 kJ
- 30.**  $\Delta G^\circ$  for a reaction is 46.06 Kcal/mole.  $K_p$  for the reaction at 300 K is  
**a.**  $10^{-33.33}$       **b.**  $10^{-8}$   
**c.**  $10^{22.22}$       **d.** None of these
- 31.** Heat of combustion of carbon monoxide at constant volume and at 17°C is -67, 710 calories. The heat of combustion at constant pressure is  
**a.** +68,900 calories  
**b.** -68,000 calories  
**c.** -67,800 calories  
**d.** -67,060 calories
- 32.** Standard heat of formation for  $\text{CCl}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and HCl at 298 K are -25.5, -57.8, -94.1 and -22.1 kJ/mol respectively. For the reaction
- $$\text{CCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{HCl}$$
- What will be  $\Delta H$ ?  
**a.** -41.4 kJ      **b.** 45.5 kJ  
**c.** -31.4 kJ      **d.** 21.7 kJ
- 33.** The bond dissociation energies for  $\text{Cl}_2$ ,  $\text{I}_2$  and  $\text{ICl}$  are 242.3, 151.0 and 211.3 kJ/mol respectively. The enthalpy of sublimation of iodine is 62.8 kJ/mole. What is the standard enthalpy of formation for  $\text{ICl}(\text{g})$  nearly equal to?

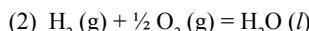
## 4.66 ■ Energetics

- a. 11.6 kJ/mole      b. -15.8 kJ/mole  
 c. 19.8 kJ/mole      d. 16.8 kJ/mole

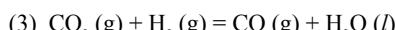
34. Consider the following reactions:



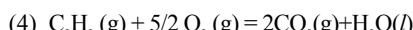
$$\Delta H = -X_1 \text{ kJ mol}^{-1}$$



$$\Delta H = -X_2 \text{ kJ mol}^{-1}$$



$$\Delta H = -X_3 \text{ kJ mol}^{-1}$$



$$\Delta H = +X_4 \text{ kJ mol}^{-1}$$

Enthalpy of formation of  $\text{H}_2\text{O(l)}$  is

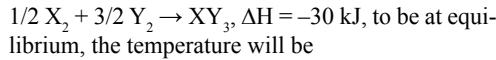
- a.  $-X_2 \text{ kJ mol}^{-1}$       b.  $+X_3 \text{ kJ mol}^{-1}$   
 c.  $-X_4 \text{ kJ mol}^{-1}$       d.  $+X_1 \text{ kJ mol}^{-1}$

35. Given that bond energies of H–H and Cl–Cl are 430  $\text{kJ mol}^{-1}$  and 240  $\text{kJ mol}^{-1}$  respectively and  $\Delta H_f$  for HCl is  $-90 \text{ kJ mol}^{-1}$ , bond enthalpy of HCl is  
 a. 290  $\text{kJ mol}^{-1}$       b. 380  $\text{kJ mol}^{-1}$   
 c. 425  $\text{kJ mol}^{-1}$       d. 245  $\text{kJ mol}^{-1}$

36. If 150 kJ of energy is needed for muscular work to walk a distance of one km. Then how much amount of glucose one has to consume to walk a distance of 5 km, provided only 30% of energy is available for muscular work. The enthalpy of combustion of glucose is 3000  $\text{kJ mol}^{-1}$ .

- a. 35 g      b. 45 g  
 c. 150 g      d. 175 g

37. Standard entropy of  $X_2$ ,  $Y_2$  and  $XY_3$  are 60, 40 and  $50 \text{ JK}^{-1} \text{ mol}^{-1}$ , respectively. For the reaction,



- a. 1250 K      b. 500 K  
 c. 750 K      d. 1000 K

38. A reversible isothermal evaporation of 90 g of water is carried out at 100°C. Heat of evaporation of water is 9.73 kcal  $\text{mol}^{-1}$ . Assuming water vapour to behave like an ideal gas, what is the change in internal energy of the system?

- a. 22.41 kcal      b. 44.82 kcal  
 c. 54.18 kcal      d. -44.48 kcal

39. An intimate mixture of ferric oxide and aluminium is used as solid fuel in rockets. Calculate the fuel value per  $\text{cm}^3$  of the mixture. Heats of formation and densities are as follow:

$$\Delta H_f(\text{Al}_2\text{O}_3) = -399 \text{ kcal mol}^{-1};$$

$$\Delta H_f(\text{Fe}_2\text{O}_3) = -199 \text{ kcal mol}^{-1}$$

$$\text{Density of Fe}_2\text{O}_3 = 5.2 \text{ g/cm}^3;$$

$$\text{Density of Al} = 2.7 \text{ g/cm}^3$$

- a. 39.4 kcal      b. 3.94 kcal  
 c. 2.42 kcal      d. 0.394

40. Calculate the enthalpy change for the process:  
 $\text{CCl}_4(\text{g}) \rightarrow \text{C(g)} + 4\text{Cl(g)}$

Calculate bond enthalpy by C – Cl in  $\text{CCl}_4(\text{g})$

C Given:

$$\Delta H^\circ \text{vap CC}l_4 = 305 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ \text{ CC}l_4 = -135.5 \text{ kJ mol}^{-1}$$

$$\Delta H_a^\circ (\text{C}) = 715 \text{ kJ mol}^{-1} \text{ (Enthalpy of atomization)}$$

$$\Delta_a^\circ \text{ H(Cl}_2) = 242 \text{ kJ mol}^{-1} \text{ (Enthalpy of atomization)}$$

- a. 326  $\text{kJ mol}^{-1}$       b. 163  $\text{kJ mol}^{-1}$   
 c. -326  $\text{kJ mol}^{-1}$       d. -163  $\text{kJ mol}^{-1}$

ANSWER KEYS	Q.	Ans.								
	1.	a	2.	b	3.	b	4.	b	5.	b
	6.	a	7.		8.	b	9.	c	10.	d
	11.	a	12.	c	13.	d	14.	b	15.	a
	16.	b	17.	c	18.	c	19.	d	20.	c
	21.	d	22.	b	23.	b	24.	a	25.	b
	26.	b	27.	d	28.	a	29	b	30.	b
	31.	a	32.	b	33.	a	34.	d	35.	a
	36.	c	37.	c	38.	c	39.	b	40.	a

## Hints and Explanations

1. As  $\Delta H = \Delta E + \Delta n RT$

$$\Delta n = -1$$

$$164 \times 10^3 = \Delta E - 1 \times 8.314 \times 298$$

$$= \Delta E - 2.478 \times 10^3$$

$$\Delta E = 164 \times 10^3 + 2.478 \times 10^3$$

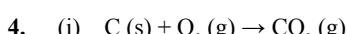
$$= 166.5 \text{ kJ mol}^{-1}$$

2. At equilibrium,  $\Delta G_{T,P} = 0 = \Delta H - T\Delta S$

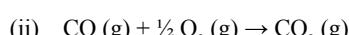
$$= (90000 - T \times 90) \text{ J.}$$

$$T = \frac{90000}{90} = 1000 \text{ K}$$

If T is > 1000 K,  $\Delta G$  will be negative and the reaction is spontaneous

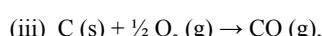


$$\Delta H = -393.5 \text{ kJ}$$



$$\Delta H = -283.0 \text{ kJ}$$

eq. (i) and (ii) gives



$$\Delta H = -110.5 \text{ kJ}$$

This equation (iii) also represents formation of one mole of CO and thus enthalpy change is the heat of formation of CO (g).

5.  $\Delta S = \frac{\Delta H}{T(K)}.$

$$14.4 = \frac{\Delta H}{390}.$$

$$\Delta H = 390 \times 14.5 = 5655 \text{ cal.mol}^{-1}$$

$$= \frac{5655}{60} = 94.25 \text{ cal g}^{-1}$$

6.  $\Delta H$  combustion for 1 mole of methane

$$= 880 \text{ kJ}$$

2640 kJ of heat will be evolved by 3 moles of methane

3 moles can occupy at STP =  $3 \times 22.4$

$$= 67.2 \text{ L}$$

9.  $W = -P\Delta V = -1.5(1 - 0.5)$

$$= -0.75 \text{ L atm}$$

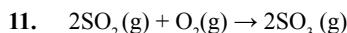
$$= -0.75 \times 101.3 \text{ J} = -75.98 \text{ J}$$

(as 1 L atm = 101.3 J)

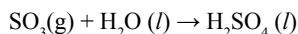
## 4.68 ■ Energetics

$$\Delta E = q + W$$

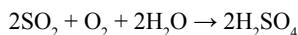
$$= 120 + (-75.98) = 44.02 \text{ J}$$



$$\Delta H = -196.7 \text{ kJ/mol}$$



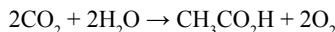
$$\Delta H = -130.1 \text{ kJ/mol}$$



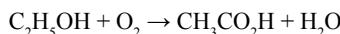
$$\Delta H = -456.9 \text{ kJ}$$



$$\Delta H = -1366.9 \text{ kJ}$$



$$\Delta H = 869.9 \text{ kJ}$$



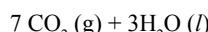
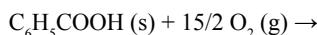
$$\Delta H = -497.0 \text{ kJ}$$



By equations (ii) + (iii) – (i), we get



14. The reaction is



$$\Delta H = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants})$$

$$= [7 \times \Delta H_f^\circ (\text{CO}_2) + 3 \times \Delta H_f^\circ (\text{H}_2\text{O})]$$

$$- [\Delta H_f^\circ (\text{C}_6\text{H}_5\text{COOH}) + 15/2 \Delta H_f^\circ (\text{CO}_2)]$$

$$= [7 \times (-393) + 3 \times (-286)] - [-408 + 0] \text{ kJ}$$

$$= -3201 \text{ kJ}$$

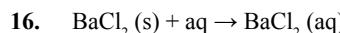
$$\text{Now } \Delta E = \Delta H - \Delta n_g RT$$

$$\Delta n_g = 7 - 15/2 = -1/2;$$

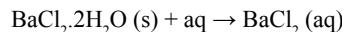
$$R = 8.314/1000 \text{ kJ mol}^{-1}$$

Putting the values, we get

$$\Delta E = -3199.9 \text{ kJ} = -3200 \text{ kJ}$$



$$\Delta H_1 = -22.8 \text{ kJ}$$



$$\Delta H_2 = +10.8 \text{ kJ}$$

$$\Delta H_3 = \Delta H_1 - \Delta H_2 = -22.8 - 10.8 = -33.6 \text{ kJ}$$



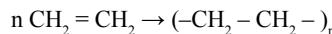
$$17. K_f = \frac{0.002 T^2 \times 128}{1}$$

$$6.9 = \frac{0.002 T^2 \times 128}{4635}$$

$$T^2 = \frac{6.9 \times 4635}{0.002 \times 128}$$

$$T = 353.45 \text{ K} = 80.45^\circ\text{C}$$

18. Polymerization reaction

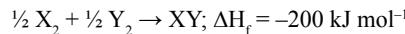


One mole of C = C bond is broken and two moles of C – C bonds are formed per mole of ethylene.

$$\Delta H = 592 - 2 \times 333$$

$$= 590 - 666 = -76 \text{ kJ per mole of ethylene}$$

19. Let the bond dissociation energy of XY, X<sub>2</sub> and Y<sub>2</sub> be as x kJ mol<sup>-1</sup>, x kJ mol<sup>-1</sup> and 0.5 × kJ mol<sup>-1</sup> respectively.



$$\Delta H_{\text{reaction}} = [( \text{sum of bond dissociation energy of all reactants}) - (\text{sum of bond dissociation energy of product})]$$

$$= [\frac{1}{2}\Delta H_{X_2} + \frac{1}{2}\Delta H_{Y_2} - \Delta H_{XY}]$$

$$= \frac{x}{2} + \frac{0.5x}{2} - x = -200$$

$$x = \frac{200}{0.25} = 800 \text{ kJ mol}^{-1}$$

$$22. w = -2.303 \times \frac{1}{2} \times 8.314 \times 300 \log_{10} \frac{35}{7}$$

$$= -2.01 \times 10^3 \text{ Joule.}$$

23. Given that

$$\Delta H = -382.64 \text{ kJ mol}^{-1}$$

$$\Delta S = -145.6 \text{ J K}^{-1} \text{ mol}^{-1} = -145.6 \times 10^{-3} \text{ kJ K}^{-1}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\text{so } \Delta G = -382.64 - (298 \times -145.6 \times 10^{-3})$$

$$= -339.3 \text{ kJ mol}^{-1}$$



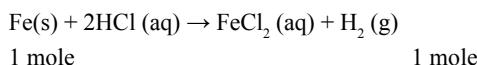
By equation [4 × eq. (ii)] – [2 × eq. (i)], we get



24.  $W = -P_{\text{ext}} \Delta V$

$$\Delta V = V_{\text{final}} - V_{\text{initial}} = V_{\text{final}} = \frac{nRT}{P_{\text{ext}}}$$

$$W = -P_{\text{ext}} \cdot \frac{nRT}{P_{\text{ext}}} = -nRT.$$

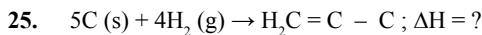


No. of moles of Fe = No. of moles of  $\text{H}_2$

$$= \frac{50}{56}$$

$$W = -\frac{50}{56} \times 8.314 \times 296$$

$$= -2212.11 \text{ J.}$$



$\Delta H = \sum \text{B.E. (reactants)} - \sum \text{B.E. (products)}$

$$= [5\text{Cs} \rightarrow \text{g} + 4\text{BE}_{\text{H-H}}] - [2\text{BE}_{\text{C-C}} + 2\text{BE}_{\text{C-C}} + 8\text{BE}_{\text{C-H}}]$$

$$= [5 \times 171 + 4 \times 104] - [2 \times 83 + 2 \times 147 + 8 \times 98.8]$$

$$= 20.6 \text{ kcal.}$$

26.  $\Delta G = \Delta H - T\Delta S = 0$

$$\Delta H = T\Delta S$$

$$T = \frac{\Delta H}{\Delta S} = \frac{-85.4 \times 1000}{-188.3} = 453.53 \text{ K.}$$

27.  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$T\Delta S^\circ = \Delta H^\circ + \Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$= \frac{-374.9 - (-305)}{298}$$

$$= \frac{-374.9 + 305}{298} = \frac{-69.9}{298}$$

$$= -0.2346 \text{ kJ/mole K}$$

$$= -234.56 \text{ J/mole K}$$

28.  $W = mgh$

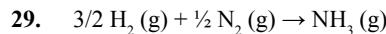
$$= 60 \text{ kg} \times 9.8 \text{ ms}^{-1} \times 100 \text{ m}$$

$$= 58800 \text{ J} = 58.8 \text{ kJ}$$

2870 kJ of heat or work is obtained = 180 g glucose

58.8 kJ of heat or work is obtained from

$$= \frac{180 \times 58.8}{2870} = 3.7 \text{ g glucose}$$



$$\Delta n = 1 \text{ mole} - 1.5 \text{ mole} - 0.5 \text{ mole}$$

$$= -1.00 \text{ mole}$$

$$RT = \frac{8.314 \times 298}{1000} = 2.48 \text{ kJ}$$

$$\Delta E = \Delta H - nRT$$

$$= 56.1 - (-1) \times 2.48$$

$$= 56.1 + 2.48 = -53.6 \text{ kJ.}$$

30.  $\Delta G^\circ = -RT \ln K_p$

$$1 \text{ cal} = 4.182 \text{ joule}$$

$$R = 8.314 \text{ J/mol}$$

$$46.06 \times 1000 \times 4.182$$

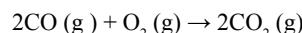
$$= -2.303 \times 8.314 \times 300 \log K_p$$

$$192622.92 = -5744.142 \log K_p$$

$$\log K_p = -33.53$$

$$\text{i. } K_p = 10^{-33.53}$$

31.  $\Delta E = -67710 \text{ cal.}$



$$\Delta n = 2 - 3 = -1$$

$$t = (273 + 17) = 290 \text{ K}$$

## 4.70 ■ Energetics

Heat of combustion at constant pressure,

$$\Delta H = \Delta E + \Delta nRT$$

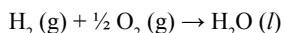
$$= -67710 + (-1) \times 2 \times 290$$

$$= -67710 - 580$$

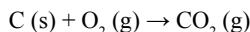
$$= -68290 \text{ cal.}$$



$$\Delta H_1 = -25.5 \text{ kJ/mol}$$



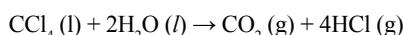
$$\Delta H_2 = -57.8 \text{ kJ/mol}$$



$$\Delta H_3 = -94.1 \text{ kJ/mol}$$

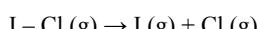


$$\Delta H_4 = -22.1 \text{ kJ/mol}$$

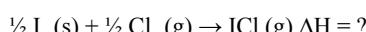


$$\Delta H = (25.5 + 2 \times 57.8 - 94.1 - 4 \times 22.1)$$

$$= -41.4 \text{ kJ}$$

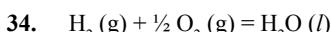


$$\Delta H_3 = 211.3 \text{ kJ/mol}$$



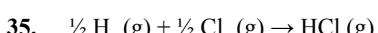
$$\Delta H = \left[ \frac{62.8 + 151.0 + 242.3}{2} - \frac{211.3}{1} \right]$$

$$= 228.05 - 211.3 = 16.75 \text{ kJ/mol}$$



$$\Delta H = -X_2 \text{ kJ mol}^{-1}$$

This reaction represents the enthalpy of formation of  $\text{H}_2\text{O} (\text{l})$ .



$$\Delta_f H = -90 \text{ kJ mol}^{-1}$$

$$\Delta_f H = \frac{1}{2} \text{BE} (\text{H}_2) + \frac{1}{2} \text{BE} (\text{Cl}_2) - \text{BE} (\text{HCl})$$

$$-90 = \frac{1}{2} (430) + \frac{1}{2} (240) - \text{BE} (\text{HCl})$$

$$\text{BE} (\text{HCl}) = 215 + 120 + 90 = 425 \text{ kJ mol}^{-1}$$

36. Energy consumed for walking a distance of 5 km =  $150 \times 5 = 750 \text{ kJ}$

1 mole of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$  (180 g) gives theoretically energy = 3000 kJ

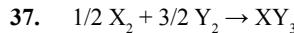
$$\text{Actual energy available} = \frac{30}{100} \times 3000$$

$$= 900 \text{ kJ}$$

As, For 900 kJ of energy, glucose required = 180 g

So, for 750 kJ of energy, glucose required

$$= \frac{180}{900} \times 750 \text{ g} = 150 \text{ g}$$



$$\Delta S_{\text{reaction}} = 50 - (3/2 \times 40 + 1/2 \times 60)$$

$$= -40 \text{ J mol}^{-1}$$

$$\Delta G = \Delta H - T\Delta S$$

As at equilibrium  $\Delta G = 0$ .

$$\text{So } \Delta H = T\Delta S$$

$$30 \times 10^3 = T \times 40$$

On solving, we get

$$T = 750 \text{ K.}$$

38. Change in enthalpy ( $\Delta H$ )

= Heat of evaporation  $\times$  Number of moles

$$= 9.73 \times 5 = 48.65 \text{ kcal}$$

$$\text{As } \Delta H = \Delta E + \Delta nRT$$

$$\text{So } \Delta E = 48.65 - (5 \times 2 \times 10^{-3} \times 373)$$

$$= 44.82 \text{ kcal.}$$

39. The required equation is:



$$\Delta H = \Delta H_{f(\text{products})} - \Delta H_{f(\text{reactants})}$$

$$= [\Delta H_f (\text{Al}_2\text{O}_3) + 2\Delta H_f (\text{Fe})] - [2\Delta H_f (\text{Al}) + H_f (\text{Fe}_2\text{O}_3)]$$

$$= [-399 + 2 \times 0] - [2 \times 0 + (-199)]$$

$$= -399 + 199 = -200 \text{ kcal}$$

At. mass of aluminium = 27,

Mol. mass of  $\text{Fe}_2\text{O}_3$  = 160

$$\text{Volume of reactants} = \frac{160}{5.2} + \frac{2 \times 27}{2.7}$$

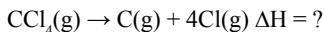
$$= 50.77 \text{ cm}$$

$$\text{Fuel value per cm}^3 = \frac{200}{5077}$$

$$= 3.94 \text{ kcal}$$

40. (i)  $\text{CCl}_4 \rightarrow \text{CCl}_4(\text{g}) \Delta H^\circ = +30.5 \text{ kJ mol}^{-1}$
- (ii)  $\text{C(s)} + 2\text{Cl}_2(\text{g}) \rightarrow \text{CCl}_4(\text{g})$   
 $\Delta H^\circ = -135.5 \text{ kJ mol}^{-1}$
- (iii)  $\text{C(s)} \rightarrow \text{C(g)} \Delta H^\circ = +715 \text{ kJ mol}^{-1}$
- (iv)  $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl(g)} \Delta H^\circ = +242 \text{ kJ mol}^{-1}$

Required equation



Equation (iii) + 2 × Equation (iv) – Equation (ii)  
– Equation (i) gives the required equation

$$\Delta H = 715 + 2(242) - 30.5 - (-135.5)$$

$$= 1304 \text{ kJ mol}^{-1}$$

$$\text{Bond enthalpy of (C-Cl) bond} = \frac{1304}{4}$$

$$= 326 \text{ kJ mol}^{-1}$$

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# CHAPTER 5 A

# Chemical Equilibrium

## Chapter Contents

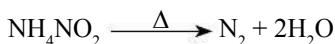
Law of mass action; Equilibrium constant, Le Chatelier's principle (effect of concentration, temperature and pressure); Significance of  $\Delta G$  and  $\Delta G^\circ$  in chemical equilibrium; and Various levels of multiple-choice questions.

### Type of Reactions

Chemical reactions are of two types:

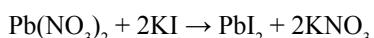
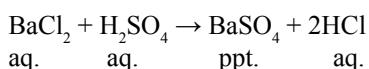
**Irreversible Reaction:** Such reactions occur in one direction only and get completed.

Example, (i) When unreactive products or solid products are formed

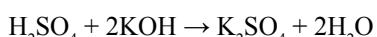


(ii) All precipitate reactions are irreversible

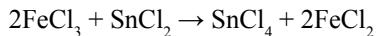
Example,



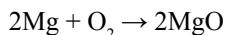
(iii) Neutralization reactions are also irreversible:



(iv) Redox reactions are also irreversible:

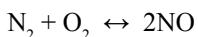


(v) Combustion reactions are also irreversible:



**Reversible Reactions:** Such reactions occur in both directions i.e., forward and backward direction however never complete as the products can give back the reactants under same or different conditions.

Example,



■ Vapourization of water in open flask is irreversible reaction while in closed flask it is reversible

■ Decomposition of  $\text{CaCO}_3$  in open flask is irreversible reaction while in closed flask it is reversible.

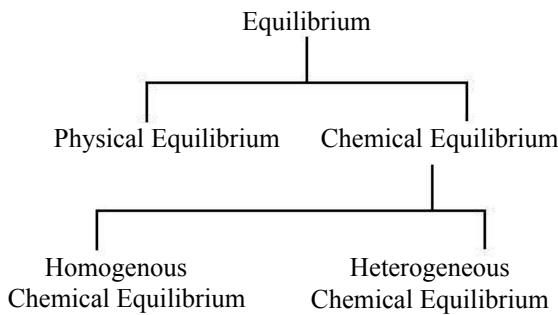
## 5.2 ■ Chemical Equilibrium

### Differences between Reversible and Irreversible Reactions:

Reversible Reaction	Irreversible Reaction
It takes place in forward as well as in backward directions.	It takes place only in forward direction.
It can never be completed.	It may be completed.
Equilibrium state can be attained.	Equilibrium state is never attained.
The change in free energy ( $\Delta G$ ) is zero.	The change in free energy is negative i.e., $\Delta G < 0$ .

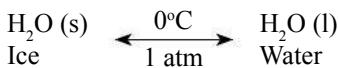
## EQUILIBRIUM

The word “equilibrium” in physical sense is explained as the “No change of state of the body”. When the two opposing process (reaction) occur simultaneously with equal rates, the system is in the state of equilibrium. Equilibrium is classified as follows

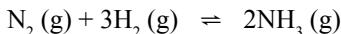


When an equilibrium exists between same chemical species, it is called physical equilibrium.

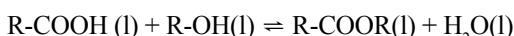
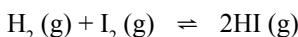
Example,



When an equilibrium exists between different chemical species, it is called chemical equilibrium.



If a chemical equilibrium has only one phase, it is called homogenous and if more than one phase it is called heterogeneous.



Phase = 1. Homogenous chemical equilibrium



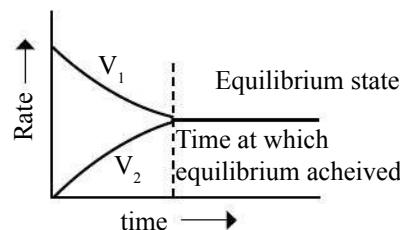
Phase = 3. Heterogeneous chemical equilibrium

## CHEMICAL EQUILIBRIUM

It is defined as: “It is the stage of a reversible reaction at which the active masses of the reactants and the products become constant in mixture and do not change with time” and rate of forward reaction is equal to that of backward reaction.

Or

“It is the state of a reversible reaction at which measurable properties like colour, density, pressure concentration are nearly unchangeable.”



Here V<sub>1</sub> and V<sub>2</sub> are rate of forward and backward reactions respectively.

i.e., Equilibrium is the state in a reversible reaction at which the rate of forward and backward reactions or two opposing reactions are same.

### Features of Chemical Equilibrium

- It is obtained only when reversible reaction is carried out in a closed space.
- Here rate of forward reaction is equal to rate of backward reaction.
- Here both forward and backward reactions are taking place with same rate hence the relative amounts of the reactants and products present at equilibrium does not change with time.
- At constant temperature it is characterized by properties like colour, density, pressure etc.
- It is possible from both the sides.
- It is dynamic in nature. It means the reaction or process is not going to be ceased as reaction occurs in both directions with equal rates.
- A catalyst cannot alter the position of equilibrium as it accelerates both the forward and backward

reactions to the same extent this means the same state of equilibrium is reaction i.e., a positive catalyst can set up equilibrium in less time but can not change it.

- At equilibrium  $\Delta G$  is equal to zero i.e.,

$$\Delta G = \Delta H - T\Delta S$$

So

$$\Delta H = T\Delta S$$

- Under the similar conditions of temperature concentration and pressure, the same state of equilibrium is reached.

Example,

When an equimolar mixture of  $H_2$  and  $I_2$  is heated to 713 K, 80% of this mixture changes into the product ( $HI$ ) and if product is again heated as 713 K only 20 % of it changes into  $H_2$  and  $I_2$

### Active Mass or Molar Concentration

It means the concentration of the reactant expressed in moles per litre or the pressure of a reacting gas in atmosphere. It is usually denoted by putting the symbol of the reactant in square bracket. E.g.,  $[A]$ .

$$C_A \text{ or } [A] = \frac{w}{m \times V \text{ (lit)}} .$$

$$(A) = \gamma \times \text{molarity}$$

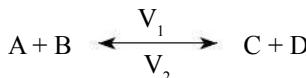
Here  $\gamma$  is the activity coefficient

In case of very dilute solution,  $\gamma$  is one. This means we can used molarity.

- Its unit is mol lit<sup>-1</sup>.
- At constant temperature  
Partial pressure  $\propto$  Active mass
- Active mass of a pure solid or a pure liquid is assumed to be one.
- Active mass of any gas at N.T.P. is 1/22.4.

### Law of Mass Action

It was introduced by Guldberg and Waage. It states that “the rate at which a substance reacts is directly proportional to its active mass(effective molar concentration) and the rate at which substances react together is directly proportional to the product of their active masses” each raised to a power which is equal to the corresponding stoichiometric number the substance present in the chemical reaction.



If active masses of A, B, C and D are  $[A]$ ,  $[B]$ ,  $[C]$ ,  $[D]$  respectively then

$$\text{Rate of reaction of A} \propto [A]$$

$$\text{Rate of reaction of B} \propto [B]$$

$$V_1 \propto [A][B] = K_1 [A][B]$$

$$V_2 \propto [C][D] = K_2 [C][D]$$

Law of mass action is not applicable for solids as for them active mass is always one.

Example,  $KClO_3 \rightarrow 2KCl + 3O_2$   
Solid

### Reaction Quotient or Concentration Quotient (Q):

It is defined as the ratio of concentration of product upon the reacting species at any point of time other than the equilibrium stage. It can be determined as follows:

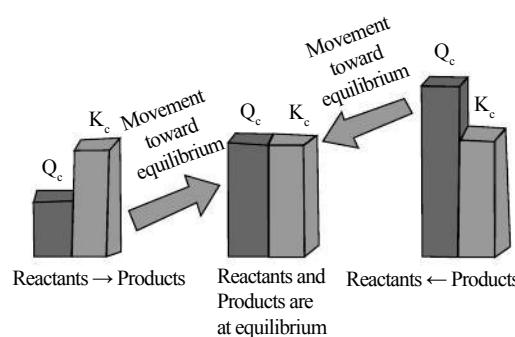
If we consider a reaction

$$m_1 A + m_2 B \leftrightarrow n_1 C + n_2 D \text{ than}$$

$$Q = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}}$$

Q can be denoted as  $Q_c$  or  $Q_p$  if we use concentration in terms of mole per litre or partial pressure respectively.

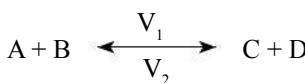
- When  $[C]^{n_1} [D]^{n_2} = [A]^{m_1} [B]^{m_2}$ .  
 $Q = K$  (reaction is at equilibrium and rate of forward and backward reactions are equal).
- When  $Q > K$  here reaction will proceed or favour backward direction this means product changes into reactant to attain equilibrium.
- When  $Q < K$  (here reaction will proceed or favour forward direction i.e., reactant changes into product to attain equilibrium).



## Equilibrium Constant

It is the ratio of rate of forward and backward reaction at a particular temperature or It is the ratio of active masses of the reactants to that of active masses of products at a particular temperature. It is denoted by  $K_c$  or  $K_p$ . The distinction between  $K_{eq}$  and  $K_c$  is that expression of  $K_{eq}$  involves all the species (whether they are pure solids, pure liquids, gases, solvents or solutions) while the expression  $K_c$  involves only those species whose concentration is a variable (gases and solution). It means  $K_c$  is a devoid of pure components (like pure solids and pure liquids) and solvents.

For a reaction



$$V_1 \propto [A][B] \text{ or } = K_1 [A][B]$$

$$V_2 \propto [C][D] \text{ or } = K_2 [C][D]$$

We know that at equilibrium  $V_1 = V_2$

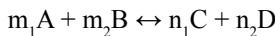
$$\text{So } K_1 [A][B] = K_2 [C][D]$$

$$\frac{K_1}{K_2} = \frac{[C][D]}{[A][B]}$$

$$K_c = \frac{[C][D]}{[A][B]} \text{ or } \frac{\text{[product]}}{\text{[reactant]}} \text{ at const temp.}$$

or

For a reaction given below equilibrium constant can be given as



$$K_c = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}}$$

### REMEMBER

Completion of reaction  $\propto K_c$

Stability of reaction  $\propto 1/K_c$

Stability of product  $\propto K_c$

## Factors Effecting Equilibrium Constant

$K_c$  does not depend upon:

- Initial concentration or pressure of reactants and products involved.

■ The presence of a catalyst.

■ The presence of an inert gas material.

■ The direction from which equilibrium has been set up.

**$K_c$  depends upon:** Equilibrium constant depends upon following factors.

### 1. Temperature

The variation of equilibrium constant with temperature is given by Van't Hoff equation as follows:

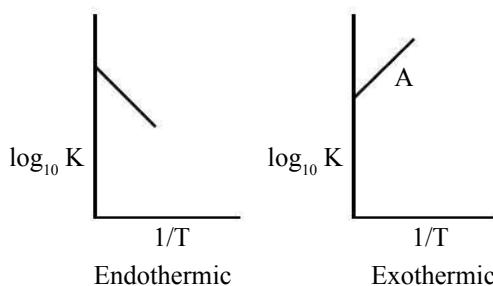
$$K = Ae^{-\Delta H^\circ / RT}$$

$$\log_{10} \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303 R} \frac{(T_2 - T_1)}{T_1 \cdot T_2}$$

$$K \propto T \quad (\Delta H = +ve)$$

$$K \propto 1/T \quad (\Delta H = -ve)$$

When a graph is plotted between  $\log_{10} K$  and  $1/T$  a straight line will be formed and the slope is equal to  $\frac{-\Delta H^\circ}{2.303R}$ .



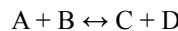
■ In case of  $\Delta H = 0$ , equilibrium constant does not depend upon temperature.

■ In case of  $\Delta H =$  positive or endothermic reactions, equilibrium constant is more at higher temperature.

■ In case of  $\Delta H =$  negative or exothermic reactions, equilibrium constant is more at lower temperature.

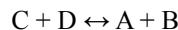
### 2. Mode of Representation of Reaction

Let us consider a reaction



$$K_c = \frac{[C][D]}{[A][B]}$$

Now if we write the above reaction as follows:



$$K_c' = \frac{[A][B]}{[C][D]}$$

i.e.,  $K_c = 1/K_c'$



$$K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]}$$



$$K_c' = \frac{[SO_2]^2 [O_2]}{[SO_3]^2} = \frac{1}{K_c}$$

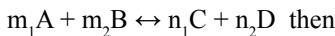
### 3. Stoichiometric Representation of Chemical Equation

Let us consider a reaction

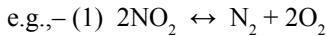


$$K_c = \frac{[C][D]}{[A][B]}$$

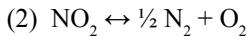
If we write the above reaction as follows:



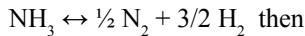
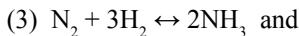
$$K_c' = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}}$$



$$\text{Here } K_c = \frac{[NO_2]^2}{[N_2][O_2]^2}$$



$$\text{Here } K_c = \frac{[NO]}{[N_2]^{1/2} [O]} = \sqrt{K_c}$$

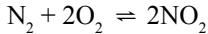
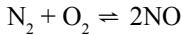


$$K_c' = 1/\sqrt{K_c}$$

### 4. Nature of reactant or product

The value of equilibrium constant also depend on the nature of reactants as well as of the products it means the value of equilibrium constant changes by changing them .

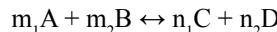
Example,



For these reaction the value of equilibrium constant differs as product differs.

### Equilibrium Constant in Terms of Partial Pressure:

If partial pressures of A, B, C, D are given as  $P_A$ ,  $P_B$ ,  $P_C$ ,  $P_D$  respectively then for the reaction  $K_p$  is given as



$$K_p = \frac{[P_C]^{n_1} [P_D]^{n_2}}{[P_A]^{m_1} [P_B]^{m_2}}$$

If we use total pressure, moles of reactant and products than  $K_p$  can be find out as follows

$$K_p = \frac{n_c^{n_1} \times n_d^{n_2}}{n_a^{m_1} \times n_b^{m_2}} \times \left( \frac{P}{\sum n} \right)^{\Delta n(g)}$$

$$\text{Here } \Delta n_g = (n_1 + n_2) - (m_1 + m_2)$$

It is interesting to know that  $K_p$  can exist only when equilibrium satisfies these two conditions.

(i) One of the reactant or the product must be in gaseous phase.

(ii) No component of the equilibrium must be present in solution phase.

### Relation between $K_p$ and $K_c$ :

$$K_p = \frac{[P_C]^{n_1} [P_D]^{n_2}}{[P_A]^{m_1} [P_B]^{m_2}}$$

$$\text{As } PV = nRT$$

$$\text{So } P = \frac{n}{V} RT$$

$$\text{As } n/V = \text{Concentration}$$

$$\text{So } P = CRT$$

$$K_p = \frac{[C]^{n_1} [RT]^{n_1} \times [D]^{n_2} [RT]^{n_2}}{[A]^{m_1} [RT]^{m_1} \times [B]^{m_2} [RT]^{m_2}}$$

$$= \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}} [RT]^{(n_1 + n_2) - (m_1 + m_2)}$$

$$K_p = K_c \cdot (RT)^{(n_1 + n_2) - (m_1 + m_2)}$$

$$\Delta n = \text{Sum of gaseous products} - \text{Sum of gaseous reactants}$$

$$\Delta n = (n_1 + n_2) - (m_1 + m_2)$$

$$K_p = K_c \cdot (RT)^{\Delta n}$$

### Units of Equilibrium Constant (K):

$$K_c = (\text{mol/lit})^{\Delta n}$$

$$K_p = (\text{atm})^{\Delta n}$$

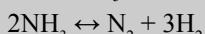
**REMEMBER**

- If  $\Delta n$  is zero  $K_p = K_c$

Here  $K_p$  and  $K_c$  have no units.



- If  $\Delta n$  is positive then  $K_p > K_c$



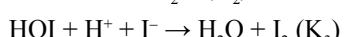
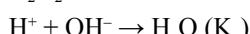
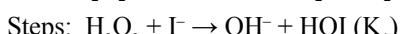
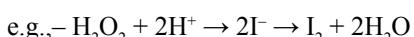
- If  $\Delta n$  is negative then  $K_c > K_p$

**Equilibrium Constant for a Multi step Reaction:**

For a multistep reaction equilibrium constant is given as

$$K = K_1 \cdot K_2 \cdot K_3$$

It means if a equilibrium reaction can be expressed as the sum of two or more equilibrium reactions, then the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.



Here  $K = K_1 \cdot K_2 \cdot K_3$

**Expressions of  $K_c$  and  $K_p$  for Some Reactions****(i) Evaluation of  $K_c$  and  $K_p$  for HI formation**

	$H_2(g)$	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Initially	a mole	b mole		0 mole
At eq.	$(a - X)$	$(b - X)$		$2X$ mole

Molar concentration or active mass of the various species at equilibrium will be

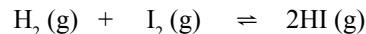
$$[H_2] = \frac{a - X}{V} \text{ m L}^{-1}$$

$$[I_2] = b - \frac{X}{V} \text{ m L}^{-1}$$

$$[HI] = \frac{2X}{V} \text{ m L}^{-1}$$

According to law of mass action

$$K_c = \frac{[HI]^2}{[H_2][I_2]} \\ = \frac{4X^2}{(a - X)(b - X)} .$$

**Evaluation of  $K_p$ :**

Initially	a mole	b mole	0 mole
At eq.	$(a - X)$	$(b - X)$	$2X$ mole

$$\text{Total number of moles} = (a - X) + (b - X) + 2X \\ = a + b$$

Partial pressure of the three species can be calculated as:

$$P(H_2) = \frac{(a - X) P}{(a + b)}$$

$$P(I_2) = \frac{(b - X) P}{(a + b)}$$

$$P(HI) = \frac{(2X) P}{(a + b)}$$

On substituting the values in the law of mass action

$$K_p = \frac{(P_{HI})^2}{(P_{H2})(P_{I2})} \\ = \frac{4X^2}{(a - X)(b - X)} .$$

**(ii) In case of NO formation:** Following the process used in HI formation, we get

$$K_c = \frac{4x^2}{(a-x)(b-x)} .$$

$$K_p = \frac{4x^2}{(a-x)(b-x)} .$$

**(iii) In case of  $NH_3$  formation:**

$$K_c = \frac{4x^2 v^2}{27(a-x)^4} .$$

or 1

$$K_p = \frac{16x^2 (2-x)^2}{27(1-x)^4 P^2} .$$

or 1

**(iv) In case of  $PCl_5$  dissociation:**

$$K_c = \frac{x^2}{(a-x)V} .$$

$$K_p = \frac{P x^2}{(1-x^2)} .$$

## Illustrations

1. At 440°C the equilibrium constant (K) for the following reaction is 49.5.



If 0.2 mole of H<sub>2</sub> and 0.2 mole of I<sub>2</sub> are placed in a 10 L vessel and permitted to react at this temperature. What will be the concentration of each substance at equilibrium?

<b>Solution</b>	H <sub>2</sub> (g)	+	I <sub>2</sub> (g)	=	2HI(g)
	0.2		0.2		0
	0.2 - X		0.2 - X		2X

Initially  
At eq.

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} .$$

$$= \frac{(2X)^2}{(0.2 - X)(0.2 - X)} .$$

$$49.5 = \frac{(2X)^2}{(0.2 - X)^2} .$$

On solving

$$X = 0.16$$

$$[\text{HI}] = 2 \times 0.16 \quad 2 \\ = 0.32$$

$$[\text{H}_2] = [\text{I}_2] = 0.2 - 0.16 = 0.04$$

2. 0.5 mole of hydrogen and 0.5 mole of iodine react in a 10 litre evacuated vessel at 450°C hydrogen iodide is formed. The equilibrium constant K<sub>c</sub> for the reaction is 50.

- (i) Calculate the value of K<sub>p</sub>.
- (ii) Calculate the moles of iodine which are in excess.

<b>Solution</b>	(i)	H <sub>2</sub>	+	I <sub>2</sub>	=	2HI
		1 mole	1 mole	2 mole		

$$\text{As } K_p = K_c (RT)^{\Delta n} = 50(RT)^0$$

$$\text{So } K_p = 50$$

(ii)	H <sub>2</sub>	+	I <sub>2</sub>	=	2HI
	0.5		0.5		0
	0.5 - X		0.5 - X		2X

Initially  
At eq.

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} .$$

$$= \frac{(2X)^2}{(0.5 - X)(0.5 - X)} .$$

$$\frac{50}{4} = \frac{(X)^2}{(0.5 - X)^2} .$$

$$\frac{X}{0.5 - X} = 3.53$$

$$X = 0.39$$

$$\text{Excess of iodine} = 0.5 - 0.39 = 0.11 \text{ moles}$$

3. One mole of H<sub>2</sub>, two moles of I<sub>2</sub> and three moles of HI are injected in a one litre flask. What will be the concentration of H<sub>2</sub>, I<sub>2</sub> and HI at equilibrium at 490°C? The equilibrium constant for the reaction at 490°C is 45.9.

<b>Solution</b>	[H] <sub>2</sub>	= 1, [I] <sub>2</sub>	= 2, [HI]	= 3 mole L <sup>-1</sup>
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Suppose X mole of H<sub>2</sub> and X mole of I<sub>2</sub> reacted at equilibrium, then

H <sub>2</sub>	+	I <sub>2</sub>	=	2HI
1 - X		2 - X		3 + 2X

At eq.

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} .$$

$$45.9 = \frac{(3 + 2X)^2}{(1 - X)(2 - X)} .$$

On solving, we get

$$X = 0.684$$

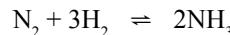
At equilibrium

$$[\text{H}_2] = 1 - X = 1 - 0.684 = 0.316 \text{ mole L}^{-1}$$

$$[\text{I}_2] = 2 - X = 2 - 0.684 = 1.316 \text{ mole L}^{-1}$$

$$[\text{HI}] = 3 + 2X = 3 + (2)(0.684) = 4.368 \text{ mole L}^{-1}$$

4. The concentration equilibrium constant, K<sub>c</sub> for the reaction

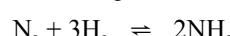


At 400 K is 0.5. Find K<sub>p</sub>

$$(R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})$$

<b>Solution</b>	K <sub>p</sub>	= K <sub>c</sub> (RT) <sup>Δn</sup>
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For the equilibrium



$$K_c = 0.5, T = 400 \text{ K}$$

$$\Delta n = 2 - (1 + 3) = -2$$

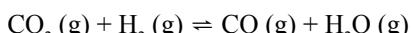
## 5.8 ■ Chemical Equilibrium

$$R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$K_p = (0.5) \times (0.082 \times 400)^{-2}$$

$$= \frac{0.5}{(32.8)^2} = 4.65 \times 10^{-4} \text{ atm}^{-2}$$

5. For the reaction,



At 1100 K and  $1.02 \times 10^5 \text{ N m}^{-2}$  pressure, the partial pressure of  $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{CO}$  are  $2.18 \times 10^4$ ,  $2.58 \times 10^4$  and  $2.72 \times 10^4 \text{ N m}^{-2}$  respectively. Find the  $K_p$  for the reaction.

**Solution**  $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$

$$K_p = \frac{P_{\text{CO}} \times P_{\text{H}_2\text{O}}}{P_{\text{CO}_2} \times P_{\text{H}_2}}$$

Partial pressure of  $\text{H}_2\text{O}(\text{g})$

$$= 1.02 \times 10^5 - (2.18 \times 10^4 + 2.58 \times 10^4 + 2.72 \times 10^4)$$

$$= 2.72 \times 10^4$$

So

$$K_p = \frac{2.72 \times 10^4 \times 2.72 \times 10^4}{2.18 \times 10^4 \times 2.58 \times 10^4}$$

$$= 1.3154$$

6. For the reaction  $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ . The equilibrium concentration of  $\text{H}_2$ ,  $\text{I}_2$  and  $\text{HI}$  are 8.0, 3.0 and 28.0 mol/l per litre respectively. Calculate the equilibrium constant of the reaction.

**Solution**  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

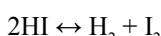
$$8.0 \quad 3.0 \quad 28.0 \text{ molar conc.}$$

at eq.

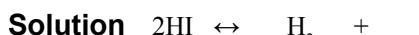
$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(28.0)^2}{8.0 \times 3.0} .$$

$$= 32.66.$$

7. Find the value of  $K_p$  for dissociation of



If the equilibrium concentration of  $\text{HI}$ ,  $\text{H}_2$  and  $\text{I}_2$  are 3.53, 0.4789 and 0.4789 mole litre<sup>-1</sup> respectively.



3.53      0.4789      0.4789 molar conc.  
at eq.

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{0.4789 \times 0.4789}{[3.53]^2}$$

$$= 1.84 \times 10^{-2}$$

$$K_p = K_c (RT)^{\Delta n}$$

Here  $\Delta n = 0$

$$K_p = K_c = 1.814 \times 10^{-2}$$

8. A gaseous mixture contains 0.30 mol  $\text{CO}$ , 0.10 mol  $\text{H}_2$  and 0.2 mol  $\text{H}_2\text{O}$ , plus an unknown amount of  $\text{CH}_4$  in each litre. This mixture is in equilibrium at 1200 K.



What is the concentration of  $\text{CH}_4$  in this mixture? The equilibrium constant,  $K_c = 3.92$ .

**Solution**  $\text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$

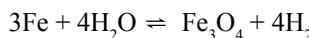
$$\begin{array}{cccc} 0.30 & 0.10 & X & 0.2 \text{ eq. moles} \\ \underline{0.30} & \underline{0.10} & \underline{X} & \underline{0.2} \text{ eq. conc.} \\ 1 & 1 & 1 & 1 \end{array}$$

$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3}$$

$$3.92 = \frac{X \times 0.2}{0.30 \times (0.10)^3} .$$

$$X = 5.88 \times 10^{-3} \text{ mol litre}^{-1}$$

9. Iron filings and water were placed in a 5.0 liter tank and sealed. The tank was heated to 1000°C. Upon analysis the tank was found to contain 1.10 g of hydrogen and 42.50 g of water vapour. The following reaction occurred in the tank:



Calculate the equilibrium constant for the reaction.

$$\text{Solution} \quad K = \frac{[\text{Fe}_3\text{O}_4][\text{H}_2]^4}{[\text{Fe}]^3[\text{H}_2\text{O}]^4}$$

$$K = \frac{k[\text{H}_2]^4}{k_1[\text{H}_2\text{O}]^4} .$$

Here  $k$  and  $k_1$  are the concentrations of  $[Fe_3O_4]$  and  $[Fe]$  respectively.

$$\text{Or } K \times \frac{k_1}{k} = K^1 = \frac{[H_2]^4}{[H_2O]^4}$$

$$[H_2] = \frac{1.10/2.02}{5.0} = 0.11 \text{ moles per litre}$$

$$[H_2O] = \frac{42.50/18.02}{5.0} = 0.47 \text{ mole per litre}$$

$$K^1 = \frac{(0.11)^4}{(0.47)^4} = 0.0030.$$

10. The  $K_p$  value for the reaction:

$H_2 + I_2 \rightleftharpoons 2HI$ , at  $460^\circ\text{C}$  is 49. If the initial pressure of  $H_2$  and  $I_2$  is 0.5 atm respectively. Determine the partial pressure of each gas at equilibrium.

### Solution

	$H_2$	+	$I_2$	$\rightleftharpoons$	$2HI$
Initial pr.	0.5		0.5		0
At. eq.	$(0.5 - X)$		$(0.5 - X)$		$2X$

$$K_p = \frac{(2X)^2}{(0.5 - X)^2} = 49$$

$$\frac{2X}{0.5 - X} = 7$$

$$2X = 3.5 - 7X$$

$$9X = 3.5$$

$$X = \frac{3.5}{9} = 0.389$$

At equilibrium:

$$P'H_2 = 0.5 - 0.389 = 0.111 \text{ atm}$$

$$PI_2 = 0.5 - 0.389 = 0.111 \text{ atm}$$

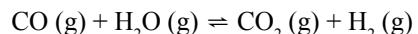
$$PHI = 0.389 \times 2 = 0.778 \text{ atm}$$

11.  $K_p$  for  $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$  at  $986^\circ\text{C}$  is 0.63. A mixture of 1 mole  $H_2O(g)$  and 3 mole  $CO(g)$  is allowed to react to come to an equilibrium. The equilibrium pressure is 2.0 atm.

- How many moles of  $H_2$  are present at equilibrium?
- Calculate partial pressure of each gas at equilibrium.

### Solution

(i)



Initial mole	3	1	0	0
--------------	---	---	---	---

Mole at eq. (3 - X)	$(1 - X)$	X	X
---------------------	-----------	---	---

Total mole at equilibrium

$$= 3 - X + 1 - X + X + X = 4$$

$$K_p = \frac{X^2}{(3 - X)(1 - X)}$$

$$0.63 = \frac{X^2}{3 + X^2 - 4X} \text{ (as } K_p = 0.63)$$

$$X = 0.681$$

$$\text{Mole of } H_2 \text{ formed} = 0.681$$

- (ii) Total pressure at equilibrium = 2 atm

Total mole at equilibrium = 4

$P'_{g} = P_M \times \text{mole fraction of that gas}$

$$P'CO_2 = PH_2 = \frac{X \cdot P}{4}$$

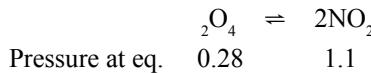
$$= \frac{0.681 \times 2}{4} = 0.34 \text{ atm}$$

$$P'CO = \frac{(2 - X) P}{4} = 1.16 \text{ atm}$$

$$P'H_2O = \frac{(1 - X) P}{4} = 0.16 \text{ atm}$$

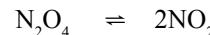
12. An equilibrium mixture at  $300 \text{ K}$  contains  $N_2O_4$  and  $NO_2$  at 0.28 and 1.1 atmosphere respectively. If the volume of container is doubled, calculate the new equilibrium pressure of two gases.

### Solution



$$K_p = \frac{(PNO_2)^2}{PN_2O_4} = \frac{(1.1)^2}{0.28} = 4.32 \text{ atm}$$

If volume of container is doubled i.e., pressure decreases and will become half, the reaction will proceed in the direction where the reaction shows an increase in mole i.e., decomposition of  $N_2O_4$  is favoured.



$$\text{New pressure at eq. } \frac{(0.28 - P)}{2} \quad \frac{(1.1 + 2P)}{2}$$

## 5.10 ■ Chemical Equilibrium

Here reactant  $\text{N}_2\text{O}_4$  equivalent to pressure P is used up in doing so.

$$K_p = \frac{[(1.1 \setminus 2) + 2P]^2}{[(0.28/2) - P]} = \frac{[0.55 + 2P]^2}{[0.14 - P]} = 4.32$$

$$P = 0.045$$

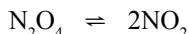
$$PN_2\text{O}_4 = 0.14 - 0.045 = 0.095 \text{ atm}$$

$$P\text{NO}_2 \text{ at new equilibrium} = 0.55 + 2 \times 0.045$$

$$P\text{NO}_2 = 0.64 \text{ atm.}$$

13. At  $25^\circ\text{C}$  and 1 atmospheric pressure, the partial pressures in equilibrium mixture of gaseous  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  are 0.7 and 0.3 atm respectively. Calculate the partial pressures of these gases when they are in equilibrium at  $25^\circ\text{C}$  and a total pressure of 10 atm.

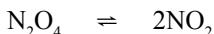
### Solution



$$\text{Pressure at eq.} \quad 0.7 \quad 0.3$$

$$K_p = \frac{(P\text{NO}_2)^2}{PN_2\text{O}_4} = \frac{0.3 \times 0.3}{0.7} = 0.1286 \text{ atm}$$

Suppose decomposition at 10 atm pressure



$$\text{Initial mole} \quad 1 \quad 0$$

$$\text{Mole at eq.} \quad (1-X) \quad 2X$$

$$K_p = \frac{(n_{\text{NO}_2})^2}{n_{\text{N}_2\text{O}_4}} \times (P/\sum n)^{\Delta n}$$

$$= \frac{(2X)^2}{(1-X)} \times [10/(1+X)]^1$$

$$1.286 = \frac{4X^2 \times 10}{(1-X^2)}$$

$$X = 0.0565$$

$$\begin{aligned} P'\text{NO}_2 &= \frac{2X}{(1+X)} \times P = \frac{2 \times 0.0565 \times 10}{(1+0.0565)} \\ &= 1.07 \text{ atm} \end{aligned}$$

$$P'\text{N}_2\text{O}_4 = \frac{(1-0.0565)}{1+0.0565} \times 10 = 8.93 \text{ atm}$$

14. At  $540 \text{ K}$ , 0.10 mole of  $\text{PCl}_5$  are heated in a 8 litre flask. The pressure of the equilibrium mixture is found to be 1.0 atm. Calculate  $K_p$  and  $K_c$  for the reaction.

### Solution

	$\text{PCl}_5$	$\rightleftharpoons$	$\text{PCl}_3$	$+$	$\text{Cl}$
Mole before diss.	0.1		0		0
Mole after diss.	(0.1-X)		X		X

Given: Volume of container = 8 litre

$$\begin{aligned} K_c &= \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(X/8) \cdot (X/8)}{(0.1-X)/8} \\ &= \frac{X^2}{8(0.1-X)} \quad \dots \dots \text{(i)} \end{aligned}$$

$$PV = nRT$$

$$1 \times 8 = (0.1+X) \times 0.082 \times 540$$

$$X = 0.08 \quad \dots \dots \text{(ii)}$$

From Equation (i) and (ii)

$$K_c = \frac{0.08 \times 0.08}{8(0.1-0.08)} = 4 \times 10^{-2} \text{ mol litre}^{-1}$$

$$K_p = K_c (RT)^{\Delta n}$$

$$\text{As } \Delta n = +1$$

$$= 4 \times 10^{-2} \times (0.082 \times 540)$$

$$= 1.77 \text{ atm}$$

15. At some temperature and under a pressure of 4 atm,  $\text{PCl}_5$  is 10 % dissociated. Calculate the pressure at which  $\text{PCl}_5$  will be 20 % dissociated, temperature remaining same.

### Solution



$$\text{Mole before diss.} \quad 0.1 \quad 0 \quad 0$$

$$\text{Mole after diss.} \quad (0.1-\alpha) \quad \alpha \quad \alpha$$

Given:  $\alpha = 0.1$  at 4 atm pressure

$$\begin{aligned} K_p &= \frac{n(\text{PCl}_3) \times n(\text{Cl}_2)}{n(\text{PCl}_5)} \times (P/\sum n)^{\Delta n} \\ &= \frac{\alpha \times \alpha}{(1-\alpha)} [P/(1+\alpha)]^1 \\ &= \frac{P\alpha^2}{(1-\alpha)} = \frac{4 \times (0.1)^2}{1-(0.1)^2} \\ K_p &= 0.040 \text{ atm} \end{aligned}$$

Again when  $\alpha$  is needed at 0.2,  $K_p$  remains constant.

$$\text{So } K_p = \frac{P\alpha^2}{1-\alpha^2}.$$

$$0.040 = \frac{P \times (0.2)^2}{1-(0.2)^2}$$

$$P = 0.96 \text{ atm}$$

### Degree of Dissociation ( $\alpha$ ):

It is the ratio of number of molecules dissociated at equilibrium to initial number of molecules.

It is given as:

$X \rightleftharpoons{} nY$	
Initial no. of moles	1      0
No. of moles at eq.	$(1 - \alpha) \quad n\alpha$

$$\text{Total number of moles at eq.} = (1 - \alpha) + n\alpha \\ = 1 + (n - 1)\alpha$$

Suppose the initial volume be  $V$  litre. Thus the volume at equilibrium

$$= [1 + (n - 1)\alpha]V.$$

Suppose 'd' is the observed vapour density at a particular temperature when degree of dissociation is ' $\alpha$ ' and D is the vapour density when there is no dissociation.

$$D \propto \frac{1}{V} \quad \dots \text{(i)}$$

$$d \propto \frac{1}{[1 + (n - 1)\alpha]V} \quad \dots \text{(ii)}$$

Dividing eq. (i) by (ii),

$$\frac{D}{d} = 1 + (n - 1)\alpha$$

$$\frac{D}{d} - 1 = (n - 1)\alpha$$

$$\frac{D}{d} - d = (n - 1)\alpha$$

$$\alpha = \frac{D - d}{(n - 1)d} .$$

$$\text{Here } D = \frac{\text{Molecular weight}}{2}$$

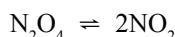
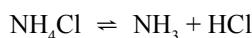
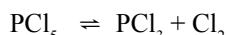
$$d = \text{Vapour density}$$

$$\alpha = M - \frac{m}{m(n - 1)} .$$

Here  $M$  = Initial molecular mass

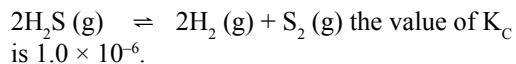
$m$  = Molecular mass at equilibrium

e.g., In the dissociation of  $\text{PCl}_5$ ,  $\text{NH}_4\text{Cl}$  and  $\text{N}_2\text{O}_4$ , the value of  $n = 2$  so



### Illustrations

16. Calculate the per cent dissociation of  $\text{H}_2\text{S}$  (g) if 0.1 mole of  $\text{H}_2\text{S}$  is kept in 0.4 litre vessel at 1000 K. For the reaction



**Solution**  $2\text{H}_2\text{S} (\text{g}) \rightleftharpoons{} 2\text{H}_2 (\text{g}) + \text{S}_2 (\text{g})$

$$\begin{array}{ccc} 0.1 - X & X & X/2 \\ V = 0.4 \text{ L} & & \end{array} \text{ At eq.}$$

$$K_c = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2}$$

$$= \frac{[X/V]^2 [X/2V]}{[(0.1 - X)/V]^2}$$

As  $X$  is very-very small so  $0.1 - X = 0.1$

$$K_c = \frac{X^3}{2V(0.1)^2} = 1.0 \times 10^{-6}$$

$$X^3 = 1.0 \times 10^{-6} \times 2 \times 0.4 \times 0.1 \times 0.1$$

$$= 8 \times 10^{-9}$$

$$X = 2 \times 10^{-3}$$

$$\% \text{ dissociation} = \frac{2 \times 10^{-3} \times 100}{0.1} \\ = 2 \%$$

17. The vapour density of  $\text{N}_2\text{O}_4$  at a certain temperature is 30. Calculate, the percentage dissociation of  $\text{N}_2\text{O}_4$  at this temperature.

**Solution** Normal molecular mass of  $\text{N}_2\text{O}_4 = 28 + 64 = 92$

Normal vapour density (V.D. before dissociation)

$$(D) = \frac{\text{Normal molecular mass}}{2} = \frac{92}{2} = 46$$

Vapour density after dissociation (d) = 30.

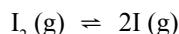


$$\text{Degree of dissociation (x)} = \frac{D - d}{d(n - 1)} .$$

$$= \frac{46 - 30}{30(2 - 1)} = \frac{16}{30 \times 1} = 0.535$$

$$x \% = 53.5$$

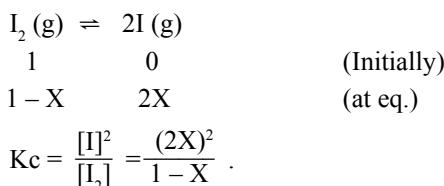
18. What is the value of  $K_c$  for the reaction,



## 5.12 ■ Chemical Equilibrium

at 1473 K, when 1 mole of  $I_2(g)$  introduced into an evacuated 1 litre flask such that only 5 % of it gets dissociated?

**Solution** For this reaction



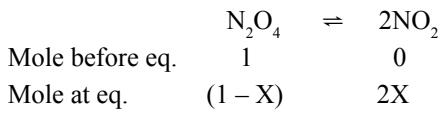
As degree of dissociation is 5 %

$$X = 0.05$$

$$\begin{aligned} \text{So } K_c &= \frac{(2 \times 0.05)^2}{1 - 0.05} \\ &= \frac{0.01}{0.95} = 0.0105 \end{aligned}$$

19. The  $K_p$  for the reaction  $N_2O_4 \rightleftharpoons 2NO_2$  is 640 mm at 775 K. Calculate the percentage dissociation of  $N_2O_4$  at equilibrium pressure of 160 mm. At what pressure, the dissociation will be 50%?

**Solution**



$$K_p = \frac{4X^2}{(1-X)} \times [P/\sum_n]^{An}$$

$$640 = \frac{4X^2}{(1-X)} \times \frac{160}{(1+X)} .$$

$$4 = \frac{4X^2}{1-X^2} .$$

$$1 - X^2 = X^2$$

$$2X^2 = 1$$

$$X^2 = \frac{1}{2}$$

$$X = 0.707 = 70.7 \%$$

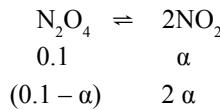
$$640 = \frac{2 \times (0.5)^2}{0.5} \times \frac{P}{1.5} . \quad (\text{as } X = 0.5)$$

$$P = 480 \text{ mm}$$

20. 0.1 mole of  $N_2O_4(g)$  was sealed in a tube under atmospheric conditions at 25°C. Calculate the number of mole of  $NO_2(g)$  present, if the equilibrium

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ , ( $K_p = 0.14$ ) is reached after some time.

**Solution**



As  $P \propto 0.1$

So  $1 \propto 0.1$

If V and T are constant

$$P \propto 0.1 + \alpha$$

$$P = [(0.1 + \alpha)/0.1]$$

$$K_p = \frac{(2\alpha)^2}{(0.1 - \alpha)} \times [P/(0.1 + \alpha)]^1$$

$$K_p = \frac{40 \alpha^2}{(0.1 - \alpha)} .$$

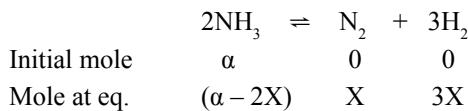
$$\frac{40 \alpha^2}{(0.1 - \alpha)} = 0.14$$

$$\alpha = 0.017$$

$$NO_2 = 0.017 \times 2 = 0.034 \text{ mole.}$$

21.  $NH_3$  is heated at 15 atm from 27°C to 347°C assuming volume constant. The new pressure becomes 50 atm at equilibrium of the reaction  $2NH_3 \rightleftharpoons N_2 + 3H_2$ . Calculate per cent of mole of  $NH_3$  actually decomposed.

**Solution**



Initial pressure of  $NH_3$  of  $\alpha$  mole

$$= 15 \text{ atm at } 27^\circ C$$

The pressure of  $\alpha$  mole of  $NH_3$

$$= P \text{ atm at } 347^\circ C$$

$$\frac{15}{300} = \frac{P}{620} .$$

$$P = 31 \text{ atm}$$

At constant volume and at 347°C

Mole  $\propto$  Pressure

$$\text{Before eq.} \quad \alpha \propto 31$$

$$\text{After eq.} \quad \alpha + 2X \propto 50$$

$$\frac{\alpha + 2X}{\alpha} = \frac{50}{31}$$

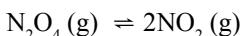
$$X = \frac{19}{62} \alpha$$

$$\% \text{ of } \text{NH}_3 \text{ decomposed} = \frac{2X}{\alpha} \times 100$$

$$= \frac{2 \times 19\alpha}{62 \times \alpha} \times 100$$

$$= 61.3 \%$$

22. (i) Find the vapour density of nitrogen tetroxide which dissociates according to this equation.



at 373 K given the degree of dissociation of  $\text{N}_2\text{O}_4$  is 0.8

- (ii) Also find the total pressure of the mixture at equilibrium (Given  $K_c = 0.2616 \text{ mole litre}^{-1}$ )

### Solution

- (i) The relationship between the degree of dissociation and the densities is given as

$$\alpha = \frac{D - D'}{D}$$

Here D = calculate vapour density

$D'$  = observed vapour density at equilibrium

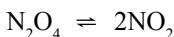
$$D \text{ of } \text{N}_2\text{O}_4 = \frac{\text{molecular weight}}{2} = \frac{92}{2} = 46$$

As  $\alpha$  is given as equal to 0.8,

$$0.8 = \frac{46 - D'}{D'}$$

$$D' = 25.56$$

$$(ii) \text{ As } K_p = K_c (RT)^{\Delta n}$$



$$\Delta n = 2 - 1 = 1$$

$$\text{So } K_p = K_c (RT)^2$$

$$= 0.2616 \times 0.082 \times 373 = 8 \text{ atm}$$

Suppose the initial concentration of  $\text{N}_2\text{O}_4$  is 1 mole.

Initial concentration of  $\text{NO}_2 = 0$

As the degree of dissociation is 0.8 equilibrium concentrations of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  are  $(1 - 0.8 = 0.2)$  and  $(2 \times 0.8 = 1.6)$  respectively.

So the total number of moles at equilibrium

$$= 0.2 + 1.6 = 1.8 \text{ mole.}$$

If P is the total pressure at equilibrium, we get

$$P_{\text{NO}_2} = \frac{2 \times 0.8}{1.8} \times P$$

$$P_{\text{N}_2\text{O}_4} = \frac{0.2}{1.8} \times P$$

$$K_p = \frac{P^2 \text{NO}_2}{P \text{N}_2\text{O}_4}$$

$$8 \text{ atm} = \frac{(2 \times 0.8/1.8)^2 P^2}{0.2 P/1.8}$$

On solving, we get

$$\text{Total pressure (P)} = 1.125 \text{ atm}$$

Relation between Standard Gibb's Free Energy and Equilibrium Constant:

Or

Van't Hoff Reaction Isotherm:

It shows the free energy change of a reaction at any given temperature, pressure and composition of the reacting system as follows:

$$\Delta G = \Delta G^\circ + RT \ln J$$

$$\text{As at equilibrium } \Delta G \text{ is } 0 \text{ so } \Delta G^\circ = -RT \ln J_{\text{eq}}$$

Here J stands for reaction quotient of partial pressures of products and reactants.

$$\frac{\text{Concentration terms of products}}{\text{Concentration terms of reactants}}$$

$J_{\text{eq}}$  means the partial pressure of the products and the reactants at the equilibrium i.e.,  $J_{\text{eq}}$  can be replaced by  $K_p$ .

$$\text{So } \Delta G^\circ = -RT \ln K_p$$

$$\Delta G^\circ = -2.303 RT \log_{10} K$$

$$\text{If } \Delta G^\circ > 0 \text{ (+ve), } K < 1$$

Backward reaction is feasible

$$\text{If } \Delta G^\circ < 0 \text{ (-ve), } K > 1$$

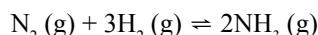
Forward reaction is feasible

$$\text{If } \Delta G^\circ = 0, K = 1$$

Equilibrium state is obtained.

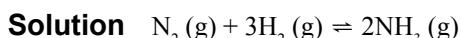
### Illustrations

23. Calculate the value of  $\log K_p$  for the reaction,



## 5.14 ■ Chemical Equilibrium

at 25°C. The standard enthalpy of formation of NH<sub>3</sub> (g) is -46 kJ and standard entropies of N<sub>2</sub> (g), H<sub>2</sub> (g), and NH<sub>3</sub> (g) are 191, 130, 192 JK<sup>-1</sup> mol<sup>-1</sup> respectively. (R = 8.3 JK<sup>-1</sup> mol<sup>-1</sup>)



At equilibrium

$$-\Delta G^\circ = 2.303 RT \log_{10} K_p \dots\dots (i)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Given: ΔH° for NH<sub>3</sub> = -46 kJ

$$\Delta S^\circ_{\text{reaction}} = 2 \times S^\circ_{\text{NH}_3} - S^\circ_{\text{N}_2} - 3 \times S^\circ_{\text{H}_2}$$

$$= 2 \times 192 - 191 - 3 \times 130$$

$$= -197 \text{ J}$$

$$T = 273 + 25 = 298 \text{ K}$$

$$\Delta G^\circ = -92 \times 10^3 - 298 \times (-197)$$

$$(\Delta H^\circ \text{ for reaction} = -46 \times 2 \text{ kJ})$$

$$= -92000 + 58706$$

$$\Delta G^\circ = -33294 \text{ J}$$

From equation (i)

$$+33294 = 2.303 \times 298 \times 8.3 \log_{10} K_p$$

$$\log_{10} K_p = 5.845.$$

24. Given values of ΔG° at 25°C for liquid ethanol (-174 kJ/mol) and gaseous ethanol (-168.6 kJ/mol), Calculate the vapour pressure of ethanol at 25°C?



$$\Delta G^\circ = [\Delta G^\circ_f (\text{C}_2\text{H}_5\text{OH}) \text{ (g)} - \Delta G^\circ_f (\text{C}_2\text{H}_5\text{OH}) \text{ (l)}]$$

$$\Delta G^\circ = (1)(-168.6) - (1)(-174.9)$$

$$= +6.3 \text{ kJ}$$

$$\Delta G^\circ = -RT \ln K$$

$$\ln K = \frac{-\Delta G^\circ}{RT}$$

$$\frac{-(6.3 \text{ kJ/mol})}{[8.314 \times 10^{-3} \text{ kJ/(K.mol)}] (298 \text{ K})} = -2.54$$

$$K = e^{-2.54} = 0.079$$

$$K = K_p = P \text{C}_2\text{H}_5\text{OH} = 0.079 \text{ atm}$$

## LE CHATELIERS PRINCIPLE

It describes the effect of change in concentration, pressure and temperature on the reversible system.

According to it, "If the system at equilibrium is subjected to a change of concentration or temperature or pressure, the system adjusts itself in such a way as to annul the effect of that change i.e., the effect of these changes can be neglected or minimized."

### Effect of Concentration

- An increase in concentration of any substance favours the reaction in which it is used up i.e., in opposite direction.
- An increase of concentration of reactant favours formation of more product i.e., forward reaction.
- Increase in concentration of product favours backward reaction i.e., its continuous removal is essential for more formation of it.

### Effect of Pressure

- High pressure is favorable for the reaction in which there is a decrease in volume or nr > np.
- Low pressure is favorable for the reaction in which there is an increase in volume or nr < np.
- Pressure is kept constant when volume is constant or nr = np.

Here nr = moles of gaseous reactant

np = moles gaseous product

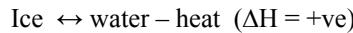
### Effect of Temperature

- Increase in temperature favours the forward reaction in the endothermic reaction (ΔH = +ve)
- Decrease in temperature favours the forward reaction in the exothermic reaction (ΔH = -ve).

### Applications of Le Chatelier's Principle

#### 1. On Physical Equilibrium

##### (i) Ice-Water System (Melting of Ice):



As it is an endothermic process and there is a decrease in volume so, the favourable conditions for melting of ice are high temperature and high pressure

**(ii) Water-Steam System (Evaporation of Water):**

Water  $\leftrightarrow$  steam – heat ( $\Delta H = +ve$ )

(As it is an endothermic process and there is a increase in volume so, the favourable conditions for evaporation of water are high temperature and low pressure.

**(iii) Solubility of Gases in Liquids:** When a gas dissolves in a liquid, there is a decrease in its volume so an increase in pressure will favour the dissolution of a gas in liquid i.e., solubility of a gas is directly proportional to partial pressure of the gas (Henry's law)

On opening carbonated water bottle,  $\text{CO}_2$  comes out as its pressure decreases.

**(iv) Effect of Temperature on Solubility:**

Exothermic substances like  $\text{CaO}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{KOH}$  are more soluble in cold water than in hot water i.e., low temperature favours their solubility.

Endothermic substances like sugar, urea are more soluble in hot water than in cold water i.e., high temperature favours their solubility.

**(v) Effect of Pressure on Boiling Point:**

On increasing pressure boiling point increases as vapour pressure decreases.

**(vi) Effect of Pressure on Melting Point:**

Solid ( $V_1$ )  $\rightleftharpoons$  Liquid ( $V_2$ )

If  $V_1 > V_2$  melting is favoured by increase of pressure so melting point decreases for such solids.

If  $V_1 < V_2$  melting is favoured by lower pressure so melting point increases for such solids.

**REMEMBER**

- Conversion of a solid into liquid, liquid into gas is favoured by high temperature in most of the cases.
- Melting of solids is accompanied by increase of volume so low pressure favours their melting while high pressure favours solidification.

**2. On Chemical Equilibrium**

**(i) Formation of Nitric Oxide:**



Here favourable conditions for formation of NO are more concentration of  $\text{N}_2$ ,  $\text{O}_2$ , constant pressure (as  $np = nr$ ) and high temperature (as it is endothermic).

**(ii) Formation of Ammonia:**



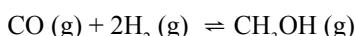
Favourable conditions for  $\text{NH}_3$  formation are more concentration of  $\text{N}_2$ ,  $\text{H}_2$ , high pressure (as  $np < nr$ ) and low temperature (as it is exothermic).

**Effect of Adding Inert Gas on Equilibrium**

- When  $np$  is equal to  $nr$  there is no effect of adding an inert gas either at constant volume or pressure.
- When  $np \neq nr$  there is no effect of adding an inert gas at constant volume.
- When  $np \neq nr$  at constant pressure on adding inert gas equilibrium will shift towards more volume side. e.g., Dissociation of ammonia will be more at constant pressure by adding inert gas like argon (Ar).

**Solved Problems from the IITs**

1. For the reaction,



hydrogen gas is introduced into a five litre flask at  $327^\circ\text{C}$ , containing 0.2 mole of  $\text{CO}(\text{g})$  and a catalyst, until the pressure is 4.92 atmosphere.

At this point 0.1 mole of  $\text{CH}_3\text{OH}(\text{g})$  is formed. Calculate the equilibrium constants  $K_p$  and  $K_c$ .

[IIT 1990]

**Solution** Let the number of moles of hydrogen introduced be 'm' moles.

## 5.16 ■ Chemical Equilibrium

Total moles of CO and hydrogen =  $0.2 + m$

As  $PV = nRT$

$$P = 4.92 \text{ atm},$$

$$V = 5 \text{ litre}$$

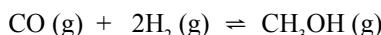
$$R = 0.082$$

$$T = (273 + 327) = 600 \text{ K}$$

$$4.92 \times 5 = 0.082 \times 600 \times (0.2 + m)$$

$$0.2 + m = \frac{4.92 \times 5}{0.082 \times 600}.$$

$$m = 0.3 \text{ mole}$$



At eq.	$0.2 - X$	$0.3 - 2X$	$X$
	$0.2 - 0.1$	$0.3 - 0.2$	$0.1$
	$= 0.1$	$= 0.1$	
Active Masses	$\frac{0.1}{5}$	$\frac{0.1}{5}$	$\frac{0.1}{5}$

According to law of mass action

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}] [\text{H}_2]^2}.$$

$$= \frac{(0.1/5)}{(0.1/5) \times (0.1/5)^2}.$$

$$= 2500 \text{ mol}^{-2} \text{ L}^2$$

$$K_p = K_c (RT)^{\Delta n}$$

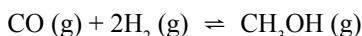
$$\text{As } \Delta n = -2$$

$$K_p = 2500 \times (0.082 \times 600)^{-2}$$

$$K_p = \frac{2500}{49.2 \times 49.2}.$$

$$= 1.0327 \text{ atm}^{-2}.$$

2. 0.15 mole of CO taken in a 2.5 litre flask is maintained at 705 K along with a catalyst so that the following reaction can take place:



Hydrogen is introduced until the total pressure of the system is 8.5 atm at equilibrium and 0.08 mole of methanol is formed. Calculate (i)  $K_p$  and  $K_c$  (ii) the final pressure if the same amount of CO and  $\text{H}_2$  as before are used, but with no catalyst so that the reaction does not take place.

**Solution** Let the total number of moles of gases be  $n$  at equilibrium.

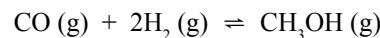
$$\text{As } PV = nRT$$

$$\text{Given } P = 8.5 \text{ atm}, V = 2.5 \text{ L}$$

$$R = 0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1}$$

$$T = 705 \text{ K}$$

$$n = \frac{8.5 \times 2.5}{0.0821 \times 705} = 0.367 \text{ mol}$$



$$\begin{array}{ccc} \text{Initial} & 0.15 & (\text{nH}_2)_0 \\ \text{mole} & & 0 \end{array}$$

$$\begin{array}{ccc} \text{At eq.} & 0.15 - X & [(\text{nH}_2)_0 - 2X] \\ & X & X = 0.08 \end{array}$$

Number of moles of CO at equilibrium

$$= 0.15 - 0.08 = 0.07 \text{ mole}$$

Number of moles of  $\text{H}_2$  at equilibrium

$$\begin{aligned} &= \text{total moles} - \text{moles of CO} - \text{moles of CH}_3\text{OH} \\ &= (0.367 - 0.07 - 0.08) \\ &= 0.217 \text{ mole} \end{aligned}$$

According to law of mass action

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}] [\text{H}_2]^2}.$$

$$= \frac{(0.08/25)}{(0.07/2.5) \times (0.217 \times 2.5)^2}.$$

$$= 151.6 \text{ mol}^{-2} \text{ L}^2$$

$$K_p = K_c (RT)^{\Delta n}$$

$$= 151.6 \times (0.0821 \times 705)^{-2}$$

$$= 0.045 \text{ atm}^2$$

$$\text{As } [(\text{nH}_2)_0 - 2X] = 0.217$$

$$(\text{nH}_2)_0 = 0.217 + 2 \times 0.08$$

$$= 0.377 \text{ mole}$$

$$(\text{n}_{\text{CO}})_0 = 0.15$$

$$\text{Total moles } (\text{n}_0) = 0.377 + 0.15 = 0.527$$

$$\text{So } p_0 = \frac{n_0 RT}{V}$$

$$= \frac{0.527 \times 0.0821 \times 705}{2.5}$$

$$= 12.20 \text{ atm.}$$

3. At temperature T, the compound  $\text{AB}_2(\text{g})$  dissociates according to the reaction,



with a degree of dissociation, X, which is small compared with unity. Deduce the expression or X in terms of the equilibrium constant,  $K_p$  and the total pressure P.

[IIT 1994]

**Solution**  $2\text{AB}_2(\text{g}) \rightleftharpoons 2\text{AB}(\text{g}) + \text{B}_2(\text{g})$

$$\text{At. eq.} \quad (1-X) \quad X \quad \frac{X}{2}$$

$$\begin{aligned} \text{Total moles at equilibrium} &= 1 - X + X + \frac{X}{2} \\ &= \frac{2+X}{2} \end{aligned}$$

$$p(\text{AB}_2) = \frac{2(1-X)}{(2+X)} \cdot P$$

$$p(\text{AB}) = \frac{2X}{(2+X)} \cdot P$$

$$p(\text{B}_2) = \frac{X}{(2+X)} \cdot P$$

$$K_p = \frac{(p_{\text{AB}})^2 (p_{\text{B}_2})}{(p_{\text{AB}_2})^2}$$

$$= \frac{[2X/(2+X)] \cdot P]^2 (X/(2+X)) \cdot P}{[2(1-X)/(2+X)] \cdot P^2}$$

$$= \frac{X^3 P}{(2+X)(1-X)^2}.$$

As X is very small,  $(2+X) = 2$  and  $(1-X) = 1$

$$\text{So } K_p = \frac{X^3 P}{2}$$

$$X^3 = \frac{2 K_p}{P}$$

$$X = (2K_p/P)^{1/3}$$

4. A sample of air consisting of  $\text{N}_2$  and  $\text{O}_2$  was heated to 2500 K until the equilibrium  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$

was established with an equilibrium constant  $K_c = 2.1 \times 10^{-3}$ . At equilibrium, the mole % of NO was 1.8. Estimate the initial composition of air in mole fraction of  $\text{N}_2$  and  $\text{O}_2$

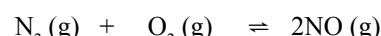
[IIT 1997]

**Solution**  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$

Let the total number of moles of  $\text{N}_2$  and  $\text{O}_2$  at initially = 100

Number of moles of  $\text{N}_2$  at initially = a

Let the number of moles of NO present at equilibrium = X



$$\text{Initially} \quad a \quad 100-a \quad 0$$

$$\text{At eq.} \quad (1-X) \quad (100-a-X) \quad 2X$$

$$\frac{2X}{100} = \frac{1.8}{100}.$$

$$X = 0.9$$

$$\text{As } K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}.$$

$$\text{So } \frac{2.1 \times 10^{-3}}{(a-X)(100-a-X)} = \frac{(2X)^2}{(a-X)(100-a-X)}.$$

$$2.1 \times 10^{-3} = \frac{(2 \times 0.9)^2}{(a-0.9)(100-a-0.9)}.$$

$$a = 79$$

% if  $\text{N}_2$  in air = 79 %

% of  $\text{O}_2$  in air =  $100 - 79 = 21\%$

5. When 3.06 g of solid  $\text{NH}_4\text{HS}$  is introduced into a two-litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.

- (i) Calculate  $K_c$  and  $K_p$  for the reaction at 27°C.  
(ii) What would happen to the equilibrium when more solid  $\text{NH}_4\text{HS}$  is introduced into the flask?

[IIT 1999]

**Solution** (i)  $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$

$$\text{Initial moles } \frac{3.06}{51} = 0.06 \quad 0 \quad 0$$

$$\text{Eq. moles } (0.06 - 0.018) \quad 0.018 \quad 0.018$$

$$\text{Molar conc. } 1 \quad \frac{0.018}{2} \quad \frac{0.018}{2}$$

$$\alpha = \frac{0.06 \times 30}{100} = 0.018$$

## 5.18 ■ Chemical Equilibrium

$$K_c = \frac{[\text{NH}_3][\text{H}_2\text{S}]}{[\text{NH}_4\text{HS}]}$$

$$= \frac{(0.018/2)^2}{1}$$

$$= 8.1 \times 10^{-5} \text{ mol L}^{-1}$$

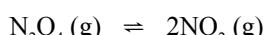
$$K_p = K_c \times (RT)^{\Delta n}$$

$$K_p = 8.1 \times 10^{-5} \times (0.082 \times 300)^2$$

$$= 0.079 \text{ atm}^2$$

(ii) Addition of  $\text{NH}_4\text{HS}$  will not effect the equilibrium position.

6. In the following equilibrium,



When 5 moles of each is taken and the temperature is kept at 298 K, the total pressure was found to be 20 bar.

$$\text{Given: } \Delta G_f^\circ (\text{N}_2\text{O}_4) = 100 \text{ kJ}$$

$$\Delta G_f^\circ (\text{NO}_2) = 50 \text{ kJ}$$

(a) Find  $\Delta G$  of the reaction at 298 K.

(b) Find the direction of the reaction.

[IIT 2004]

**Solution** Reaction quotient =  $\frac{[\text{P}(\text{NO}_2)]^2}{\text{P}(\text{N}_2\text{O}_4)}$

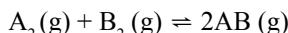
$$= \frac{100}{10} = 10$$

$$\Delta G_{\text{Reaction}}^\circ = 2 \Delta G_f^\circ (\text{NO}_2) - \Delta G_f^\circ (\text{N}_2\text{O}_4)$$

$$= 2 \times 50 - 100 = 0$$

Here negative value of  $\Delta G$  shows that reaction will be in forward direction.

7. The equilibrium constant of the reaction,



at 100°C is 50. If a one litre flask containing one mole of flask containing one mole of  $\text{A}_2$  is connected to a two litre flask containing two moles of  $\text{B}_2$ , how many moles of AB will be formed at 373 K?

[IIT 1985]

### Solution



Initially 1 2 0  
at eq.  $(1-X)$   $(2-X)$   $2X$   
(total volume = 3 lit)

Active  $\frac{(1-X)}{3}$   $\frac{(2-X)}{3}$   $\frac{2X}{3}$

According to law of mass action,

$$K_c = \frac{[\text{AB}]^2}{[\text{A}_2][\text{B}_2]} = \frac{(2x/3)^2}{(1-x)/3 \cdot (2-x)/3} = \frac{4x^2}{(1-x)(2-x)}.$$

$$\frac{4x^2}{(1-x)(2-x)} = 50$$

$$4x^2 = (2 - 3x + x^2) \times 50$$

$$2x^2 - 75x + 50 = 0$$

$$x = \frac{75 \pm \sqrt{(75)^2 - 4 \times 23 \times 50}}{2 \times 23}$$

$$x = 2.317 \text{ or } 0.934$$

The value of X cannot be more than one that is, greater than the number of moles of  $\text{A}_2$  so

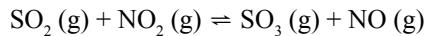
$$X = 0.943$$

$$\text{Number of moles of AB} = 2X$$

$$= (2 \times 0.934)$$

$$= 1.868$$

8. At a certain temperature, equilibrium constant ( $K_c$ ) is 16 for the reaction:



If we take one mole of each of the four gases in one litre container, what would be the equilibrium concentration of NO and  $\text{NO}_2$ ?

[IIT 1987]

**Solution**  $\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{NO}(\text{g})$

Initial 1 1 1 1  
conc.

Eq.  $(1-X)$   $(1-X)$   $1+X$   $1+X$   
conc.

According to law of mass action

$$K_c = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]}.$$

$$= \frac{(1+X)(1+X)}{(1-X)(1-X)} = 16$$

$$\frac{1+X}{1-X} = 4$$

$$1+X = 4 - 4X$$

$$5X = 3$$

$$X = 3/5 = 0.6$$

$$\begin{aligned}\text{Concentration of } \text{NO}_2 \text{ at equilibrium} &= (1-0.6) \\ &= 0.4 \text{ mole}\end{aligned}$$

$$\begin{aligned}\text{Concentration of NO at equilibrium} &= (1+0.6) \\ &= 1.6 \text{ mole}\end{aligned}$$

9.  $\text{N}_2\text{O}_4$  is 25% dissociated at  $37^\circ\text{C}$  and one atmospheric pressure. Calculate (i)  $K_p$  and (ii) the percentage dissociation at 0.1 atmospheric and  $37^\circ\text{C}$ .

[IIT 1988]

**Solution**  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

Initial	1	0
At eq.	$(1-X)$	$2X$

$$\text{Total moles} = (1-X) + 2X = (1+X)$$

$$p(\text{N}_2\text{O}_4) = \frac{(1-X)}{(1+X)} \cdot P$$

$$p(\text{NO}_2) = \frac{2X}{(1+X)} \cdot P$$

$$\text{Given } X = 0.25 \text{ and } P = 1 \text{ atm}$$

$$p(\text{N}_2\text{O}_4) = \frac{(1-0.25)}{(1+0.25)} \times 1 = 0.6 \text{ atm}$$

$$p(\text{NO}_2) = \frac{(2 \times 0.25)}{(1+0.25)} \times 1 = 0.4 \text{ atm}$$

$$K_p = \frac{(p_{\text{NO}_2})^2}{p \text{N}_2\text{O}_4} = \frac{0.4 \times 0.4}{0.6} = 0.267 \text{ atm}$$

Let the degree of dissociation of  $\text{N}_2\text{O}_4$  at 0.1 atm be 'a' then,

$$p(\text{N}_2\text{O}_4) = \frac{(1-a)}{(1+a)} \times 0.1$$

$$p(\text{NO}_2) = \frac{2a}{(1+a)} \times 0.1$$

$$K_p = \frac{\frac{(2a/1+a)^2 \times (0.1)^2}{(1-a)}}{\frac{(1-a)}{(1+a)} \times 0.1}$$

$$= \frac{4a^2 \times 0.1}{(1-a)(1+a)} = \frac{0.4 a^2}{(1-a^2)}$$

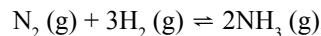
$$0.267 = \frac{0.4 a^2}{(1-a^2)}$$

$$0.267 = 0.667 a^2$$

$$a = 0.632$$

So dissociation of  $\text{N}_2\text{O}_4 = 63.2 \%$ .

10. One mole of nitrogen and three moles of hydrogen are mixed in a 4 litre container. If 0.25 % of nitrogen is converted into ammonia by the following reaction:



Find the equilibrium constant ( $K_c$ ) in concentration units. What will be the value of  $K$  for the following equilibrium?



[IIT 1989]

**Solution**  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

$$\text{At eq. } (1-X) \quad (3-3X) \quad 2X$$

$$\text{Active masses} \frac{(1-0.0025)}{4} \frac{(3-0.0075)}{4} \frac{(0.0050)}{4}$$

According to law of mass action

$$\begin{aligned}K_c &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \cdot \\ &\quad \frac{(0.0050/4)^2}{(0.9975/4)(2.9925/4)^3} \cdot \\ &= 1.49 \times 10^{-5} \text{ lit}^2 \text{ mol}^{-2}\end{aligned}$$

$K$  for the reaction,

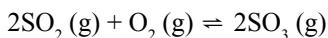


is equal to  $\sqrt{K_c}$ .

$$\begin{aligned}K &= \sqrt{K_c} = \sqrt{(1.49 \times 10^{-5})} \\ &= 3.86 \times 10^{-3} \text{ lit mol}^{-1}\end{aligned}$$

## 5.20 ■ Chemical Equilibrium

11. The equilibrium constant  $K_p$  for the reaction,

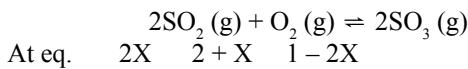


is  $900 \text{ atm}^{-1}$  at  $800 \text{ K}$ . A mixture containing  $\text{SO}_3$  and  $\text{O}_2$  having initial partial pressure of 1 and 2 atm respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at  $800 \text{ K}$ .

[IIT 1989]

**Solution** The system in the initial stage does not have  $\text{SO}_2$ .  $\text{SO}_3$  decomposes to form  $\text{SO}_2$  and  $\text{O}_2$  until equilibrium is reached. The partial pressure of  $\text{SO}_3$  decreases.

Suppose the decrease in partial pressure is  $2X$ .



According to law of mass action

$$K_p = \frac{(1-2X)^2}{(2X)^2 (2+X)}.$$

[As  $(2+X) = 2$ ]

$$900 = \frac{(1-2X)^2}{8X^2}$$

$$\frac{1-2X}{X} = 84.45$$

On solving

$$X = 0.0115 \text{ atm}$$

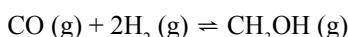
So the partial pressures at equilibrium are:

$$p(\text{SO}_2) = 2 \times 0.0115 = 0.023 \text{ atm}$$

$$p(\text{O}_2) = 2 + 0.0115 = 2.0115 \text{ atm}$$

$$p(\text{SO}_3) = 1 - 2 \times 0.0115 = 0.977 \text{ atm}$$

12. For the reaction,



hydrogen gas is introduced into a five litre flask at  $327^\circ\text{C}$ , containing 0.2 mole of  $\text{CO}(\text{g})$  and a catalyst, until the pressure is  $4.92 \text{ atmosphere}$ . At this point 0.1 mole of  $\text{CH}_3\text{OH}(\text{g})$  is formed. Calculate the equilibrium constants  $K_p$  and  $K_c$ .

[IIT 1990]

**Solution** Let the number of moles of hydrogen introduced be ‘ $m$ ’ moles.

Total moles of CO and hydrogen =  $0.2 + m$

As  $PV = nRT$

$P = 4.92 \text{ atm}$ ,

$V = 5 \text{ litre}$

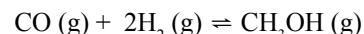
$R = 0.082$

$$T = (273 + 327) = 600 \text{ K}$$

$$4.92 \times 5 = 0.082 \times 600 \times (0.2 + m)$$

$$0.2 + m = \frac{4.92 \times 5}{0.082 \times 600}.$$

$$m = 0.3 \text{ mole}$$



$$= 0.1 = 0.1$$

$$\begin{array}{ccc} \text{Active Masses} & \frac{0.1}{5} & \frac{0.1}{5} & \frac{0.1}{5} \end{array}$$

According to law of mass action,

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}] [\text{H}_2]^2}.$$

$$= \frac{(0.1/5)}{(0.1/5) \times (0.1/5)^2}.$$

$$= 2500 \text{ mol}^{-2} \text{ L}^2$$

$$K_p = K_c (RT)^{\Delta n}$$

$$\text{As } \Delta n = -2$$

$$K_p = 2500 \times (0.082 \times 600)^{-2}$$

$$K_p = \frac{2500}{49.2 \times 49.2}.$$

$$= 1.0327 \text{ atm}^{-2}.$$

13. 0.15 mole of CO taken in a 2.5 litre flask is maintained at  $705 \text{ K}$  along with a catalyst so that the following reaction can take place:



Hydrogen is introduced until the total pressure of the system is  $8.5 \text{ atm}$  at equilibrium and 0.08 mole of methanol is formed. Calculate (i)  $K_p$

and  $K_c$  (ii) the final pressure if the same amount of CO and H<sub>2</sub> as before are used, but with no catalyst so that the reaction does not take place.

[IIT 1993]

**Solution** Let the total number of moles of gases be n at equilibrium.

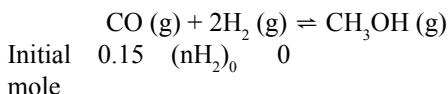
$$\text{As } PV = nRT$$

$$\text{Given } P = 8.5 \text{ atm}, V = 2.5 \text{ L}$$

$$R = 0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1}$$

$$T = 705 \text{ K}$$

$$n = \frac{8.5 \times 2.5}{0.0821 \times 705} = 0.367 \text{ mol}$$



$$\text{At eq. } 0.15 - X [(nH_2)_0 - 2X] \quad X = 0.08$$

Number of moles of CO at equilibrium

$$= 0.15 - 0.08 = 0.07 \text{ mole}$$

Number of moles of H<sub>2</sub> at equilibrium

$$= \text{total moles} - \text{moles of CO} - \text{moles of CH}_3\text{OH}$$

$$= (0.367 - 0.07 - 0.08)$$

$$= 0.217 \text{ mole}$$

According to law of mass action

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}] [\text{H}_2]^2} \cdot$$

$$= \frac{(0.08/25)}{(0.07/2.5) \times (0.217 \times 2.5)^2} \cdot$$

$$= 151.6 \text{ mol}^{-2} \text{ L}^2$$

$$K_p = K_c (RT)^{\Delta n}$$

$$= 151.6 \times (0.0821 \times 705)^{-2}$$

$$= 0.045 \text{ atm}^2$$

$$\text{As } [(n_{\text{H}_2})_0 - 2X] = 0.217$$

$$(n_{\text{H}_2})_0 = 0.217 + 2 \times 0.08$$

$$= 0.377 \text{ mole}$$

$$(n_{\text{CO}})_0 = 0.15$$

$$\text{Total moles } (n_0) = 0.377 + 0.15 = 0.527$$

$$\text{So } p_0 = \frac{n_0 RT}{V}$$

$$= \frac{0.527 \times 0.0821 \times 705}{2.5}$$

$$= 12.20 \text{ atm.}$$

14. At temperature T, the compound AB<sub>2</sub> (g) dissociates according to the reaction,



with a degree of dissociation, X, which is small compared with unity. Deduce the expression for X in terms of the equilibrium constant, K<sub>p</sub> and the total pressure P.

[IIT 1994]

**Solution** 2AB<sub>2</sub> (g) ⇌ 2AB (g) + B<sub>2</sub> (g)

$$\text{At. eq. } (1 - X) \quad X \quad \frac{X}{2}$$

$$\text{Total moles at equilibrium} = 1 - X + X + \frac{X}{2}$$

$$= \frac{2 + X}{2}$$

$$p(\text{AB}_2) = \frac{2(1 - X)}{(2 + X)} \cdot P$$

$$p(\text{AB}) = \frac{2X}{(2 + X)} \cdot P$$

$$p(\text{B}_2) = \frac{X}{(2 + X)} \cdot P$$

$$K_p = \frac{(p_{\text{AB}})^2 (p_{\text{B}_2})}{(p_{\text{AB}_2})^2}$$

$$= \frac{[\{2X/(2 + X)\} \cdot P]^2 (X/2 + X) \cdot P}{[2(1 - X)/(2 + X) \cdot P]^2}$$

$$= \frac{X^3 P}{(2 + X)(1 - X)^2} \cdot$$

As X is very small, (2 + X) = 2 and (1 - X) = 1

$$\text{So } K_p = \frac{X^3 P}{2}$$

$$X^3 = \frac{2 K_p}{P}$$

$$X = (2K_p/P)^{1/3}$$

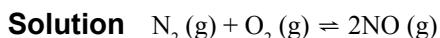
15. A sample of air consisting of N<sub>2</sub> and O<sub>2</sub> was heated to 2500 K until the equilibrium N<sub>2</sub> (g) + O<sub>2</sub> (g) ⇌ 2NO (g)

was established with an equilibrium constant K<sub>c</sub> = 2.1 × 10<sup>-3</sup>. At equilibrium, the mole % of

## 5.22 ■ Chemical Equilibrium

NO was 1.8. Estimate the initial composition of air in mole fraction of N<sub>2</sub> and O<sub>2</sub>

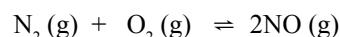
[IIT. 1997]



Let the total number of moles of N<sub>2</sub> and O<sub>2</sub> at initially = 100

Number of moles of N<sub>2</sub> at initially = a

Let the number of moles of NO present at equilibrium = X



Initially a 100 - a 0

At eq. (1 - X) (100 - a - X) 2X

$$\frac{2X}{100} = \frac{1.8}{100}.$$

$$X = 0.9$$

$$\text{As } K_c = \frac{[NO]^2}{[N_2][O_2]}.$$

$$\text{So } 2.1 \times 10^{-3} = \frac{(2X)^2}{(a - X)(100 - a - X)}.$$

$$2.1 \times 10^{-3} = \frac{(2 \times 0.9)^2}{(a - 0.9)(100 - a - 0.9)}.$$

$$a = 79$$

% if N<sub>2</sub> in air = 79 %

% of O<sub>2</sub> in air = 100 - 79 = 21 %

16. When 3.06 g of solid NH<sub>4</sub>HS is introduced into a two-litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.

- (i) Calculate K<sub>c</sub> and K<sub>p</sub> for the reaction at 27°C.  
(ii) What would happen to the equilibrium when more solid NH<sub>4</sub>HS is introduced into the flask?

[IIT 1999]



$$\begin{array}{ccccc} \text{Initial moles} & \frac{3.06 = 0.06}{51} & 0 & 0 \\ \text{Eq. moles} & (0.06 - 0.018) & 0.018 & 0.018 \end{array}$$

Molar conc.	1	0.018	0.018
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$$\alpha = \frac{0.06 \times 30}{100} = 0.018$$

$$K_c = \frac{[NH_3][H_2S]}{[NH_4HS]}$$

$$= \frac{(0.018/2)^2}{1}$$

$$= 8.1 \times 10^{-5} \text{ mol L}^{-1}$$

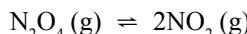
$$K_p = K_c \times (RT)^{\Delta n}$$

$$K_p = 8.1 \times 10^{-5} \times (0.082 \times 300)^2$$

$$= 0.079 \text{ atm}^2$$

(ii) Addition of NH<sub>4</sub>HS will not effect the equilibrium position.

17. In the following equilibrium,



When 5 moles of each is taken and the temperature is kept at 298 K, the total pressure was found to be 20 bar.

Given: ΔG<sub>f</sub><sup>o</sup>(N<sub>2</sub>O<sub>4</sub>) = 100 kJ

ΔG<sub>f</sub><sup>o</sup>(NO<sub>2</sub>) = 50 kJ

- (a) Find ΔG of the reaction at 298 K.  
(b) Find the direction of the reaction.

[IIT 2004]

**Solution** Reaction quotient =  $\frac{P(NO_2)^2}{P(N_2O_4)}$   
 $= \frac{100}{10} = 10$

$$\begin{aligned} \Delta G_{\text{Reaction}}^o &= 2 \Delta G_f^o(NO_2) - \Delta G_f^o(N_2O_4) \\ &= 2 \times 50 - 100 = 0 \end{aligned}$$

$$\text{As } \Delta G = \Delta G^o - 2.303 RT \log_{10} Q_p$$

$$= 0 - 2.303 \times 8.314 \times 298 \log_{10} 10$$

$$= -57.058 \text{ J}$$

$$= -5.705 \text{ kJ}$$

Here negative value of ΔG shows that reaction will be in forward direction.

## MULTIPLE-CHOICE QUESTIONS

### Straight Objective Type Questions (Single Choice only)

1. In a reaction  $A_2(g) + 4B_2(g) \rightleftharpoons 2AB_4(g)$ ;  $\Delta H < 0$ . The formation of  $AB_4(g)$  will be favoured by
  - low temperature and high pressure
  - high temperature and high pressure
  - low temperature and low pressure
  - high temperature and low pressure
2. For which of the following reaction,  $K_p = K_c$ ?
  - $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$
  - $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
  - $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$
  - $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$
3. In what manner will increase of pressure affect the following equation?  
 $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$ 
  - shift in the reverse direction
  - shift in the forward direction
  - increase in the yield of hydrogen
  - no effect
4. Which one of the following statements does not describe the equilibrium state?
  - The rate of forward reaction is equal to the rate of the reverse reaction.
  - Equilibrium is dynamic and there is no net conversion to reactants and products.
  - The concentration of the reactants is equal to the concentration of the products.
  - The concentration of the reactants and products reach a constant level.
5. Which of the following statements is false regarding the equilibrium constant,  $K_c$ ?
  - When quoting  $K_c$  it is customary to omit units.
  - The numerical value of  $K_c$  depends on the form of the balanced equation.
  - $K_c$  for a reaction at a particular temperature always has the same value.
  - $K_c$  for the reverse reaction is the negative of  $K_c$  for the forward reaction.

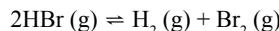
6. Which statement is true about equilibrium constant? The value of  $K_c$ 
  - remains same
  - changes as product concentration changes
  - changes as reactant concentration changes
  - changes as temperature changes.
7. Write the equilibrium equation for the forward reaction:  
 $2CH_4(g) + 3O_2(g) \rightleftharpoons 2CO(g) + 4H_2O(g)$ 
  - $K_c = \frac{[CH_4]^2 + [O_2]^3}{[CO]^2 + [H_2O]^4}$
  - $K_c = \frac{[CO]^2 [H_2O]^4}{[CH_4]^2 [O_2]^3}$
  - $K_c = \frac{2 [CH_4] + 3 [O_2]}{2 [CO] + 4 [H_2O]}$
  - $K_c = \frac{2 [CO] + 4 [H_2O]}{2 [CH_4] + 3 [O_2]}$
8. Nitric oxide reacts with oxygen to form nitrogen dioxide:  
 $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$   
 What is  $K_c'$  for the reverse reaction if the equilibrium concentration of NO is 0.300 M,  $O_2$  is 0.200 M, and  $NO_2$  is 0.530 M at  $25^\circ C$ ?
  - 0.1584
  - 6.24
  - 0.0641
  - 1.641
9. If  $K_c$  is the equilibrium constant for a forward reaction what is  $K_c'$  for the reverse reaction?
  - $1/K_c$
  - $-K_c$
  - $K_c$
  - None of these
10. Given the reaction:  
 $2HI \rightleftharpoons H_2 + I_2$ . If  $K_c'$  for the reverse reaction is  $1.85 \times 10^{-2}$  at  $425^\circ C$ , what is  $K_c$  for the forward reaction at the same temperature?
  - 58.1
  - 64.2
  - 54.1
  - 5.41
11. For the reaction  
 $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ ,

## 5.24 ■ Chemical Equilibrium

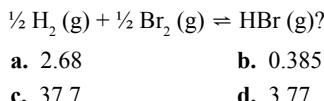
$K_c = 8.3 \times 10^{-10}$  at 25°C. What is the concentration of N<sub>2</sub> gas at equilibrium when the concentration of NO<sub>2</sub> is twice the concentration of O<sub>2</sub> gas?

- a.  $2.4 \times 10^9$  M
- b.  $4.8 \times 10^9$  M
- c.  $2.8 \times 10^9$  M
- d.  $2.8 \times 10^9$  M

12. If  $K_c = 7.04 \times 10^{-2}$  for the reaction:



What is the value of  $K_c$  for the reaction:



13. If  $K_c$  equals to 0.11 at 25°C for the reaction:  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ , what is  $K_c$  for the reaction:  $\text{NO}_2(\text{g}) \rightleftharpoons \frac{1}{2}\text{N}_2\text{O}_4(\text{g})$ ?

- a. 1.5
- b. 3.0
- c. 6.0
- d. 5.5

14. Which one of the following statements about the equilibrium constant ( $K_p$ ) is false?

- a. Total pressures are used in the equilibrium equation in place of molar concentrations.
- b. The units for  $K_p$  are usually omitted.
- c.  $\Delta n$  = the sum of the coefficients of the gaseous products – the sum of the coefficients of the gaseous reactants
- d. The relationship between  $K_p$  and  $K_c$  is:

$$K_p = K_c (\text{RT})^{\Delta n}$$

15. Given the reaction at a certain temperature

$2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ . At equilibrium, the partial pressure of HI is  $1.8 \times 10^{-3}$  atm and the partial pressures for H<sub>2</sub> and I<sub>2</sub> are 0.10 atm each. Find  $K_p$  at that temperature.

- a.  $3.1 \times 10^3$
- b.  $3.1 \times 10^{-3}$
- c.  $4.8 \times 10^4$
- d.  $2.8 \times 10^{-2}$

16. If  $K_c = 2.0 \times 10^{33}$  at 25°C, for the following reaction:

$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$ , then find  $K_p$  at the same temperature.

- a.  $3.5 \times 10^{32}$
- b.  $2.0 \times 10^{33}$
- c.  $1.8 \times 10^{33}$
- d.  $4.0 \times 10^{34}$

17. Phosphorous pentachloride decomposes to phosphorous trichloride and chlorine gas at elevated temperatures by the following reaction:

$\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ . If  $K_c = 1.8$  at 250°C, what is the value of  $K_p$  at the same temperature.

- a. 77
- b. 67
- c.  $7.7 \times 10^{-4}$
- d.  $6.7 \times 10^{-2}$

18. The decomposition of ammonia is:

$2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ . If  $K_p$  is  $1.5 \times 10^3$  at 400°C, what is the partial pressure of ammonia at equilibrium when N<sub>2</sub> is 0.10 atm and H<sub>2</sub> is 0.15 atm?

- a.  $4.1 \times 10^{-6}$  atm
- b.  $1.5 \times 10^3$  atm
- c.  $3.8 \times 10^{-4}$  atm
- d.  $4.7 \times 10^{-4}$  atm

19. The decomposition of ammonia is:

$2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ . If the partial pressure of ammonia is  $1.6 \times 10^{-3}$  atm and the partial pressures of N<sub>2</sub> and H<sub>2</sub> are each 0.25 atm at equilibrium, what is the value for  $K_c$  at 400°C for the forward reaction?

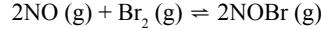
- a. 0.20
- b. 0.50
- c.  $2.8 \times 10^{-3}$
- d. 1.50

20. The decomposition of ammonia is:

$2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ . If the pressure of ammonia is  $1.0 \times 10^{-3}$  atm, and the pressures of N<sub>2</sub> and H<sub>2</sub> are each 0.20 atm, what is the value for  $K_p$  at 400°C for the reverse reaction?

- a.  $6.2 \times 10^{-4}$
- b.  $2.6 \times 10^{-4}$
- c.  $-6.2 \times 10^{-4}$
- d.  $4.2 \times 10^{-4}$

21. A 1.50 L vessel contains an equilibrium mixture of 0.100 mol of NO, 0.150 mol of Br<sub>2</sub>, and 0.250 mol of NOBr at 25°C. What is the value of  $K_p$  for the following reaction:



- a. 25.6
- b. 12.8
- c. 2.56
- d. 5.26

22. As a rule, which of the following phases are not included in the equilibrium constant expression?

- I. Pure liquids
  - II. Pure solids
  - III. Aqueous solutions
  - IV. Gases
- a. I and III
  - b. I and II
  - c. II and III
  - d. I and IV

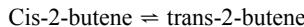
23. Which equilibrium below is homogeneous?

- a.  $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}_2(\text{g})$
- b.  $\text{NH}_4\text{NO}_3(\text{s}) \rightleftharpoons \text{N}_2\text{O}(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
- c.  $\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$
- d.  $2\text{H}_2\text{O}_2(\text{l}) \rightleftharpoons 2\text{H}_2\text{O}(\text{l}) + \text{O}(\text{g})$



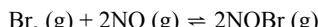
## 5.26 ■ Chemical Equilibrium

33. The equilibrium constant ( $K_p$ ) equals to 3.40 at 25°C for the isomerisation reaction:



If a flask initially contains 1.00 atm of each gas, in what direction will the system shift to reach equilibrium?

- a. The system is already at equilibrium
  - b. The system is not at equilibrium and will remain in an unequilibrated state.
  - c. It will shift left.
  - d. It will shift right.
34. At a certain temperature, bromine and nitric oxide react to form nitrosyl bromide:

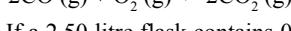


When initial amounts of  $\text{Br}_2$ , NO and  $\text{NOBr}$  are mixed, the concentration of  $\text{NOBr}$  increases. Which of the statements is true?

- a.  $K_c = Q$
  - b.  $K_c < Q$
  - c.  $K_c > Q$
  - d. More information is needed to make a statement about  $K_c$ .
35. At a certain temperature, bromine and nitric oxide react to form nitrosyl bromide:

$\text{Br}_2(\text{g}) + 2\text{NO}(\text{g}) \rightleftharpoons 2\text{NOBr}(\text{g})$ . When 0.010 mol  $\text{Br}_2$  is mixed with 0.025 mol NO and 0.015 mol  $\text{NOBr}$  in a 2.50 litre flask, the concentration of  $\text{NOBr}$  decreases. Which of the statements is true?

- a.  $K_c < 90$
  - b.  $K_c > 90$
  - c.  $K_c < 45$
  - d.  $K_c > 36$
36. At a certain temperature,  $K_c$  equals  $1.4 \times 10^2$  for the reaction:



If a 2.50 litre flask contains 0.400 mol of  $\text{CO}_2$  and 0.100 mol of  $\text{O}_2$  at equilibrium, how many moles of CO are also present in the flask?

- a. 0.169 mol
  - b. 0.238 mol
  - c. 1.69 mol
  - d. 0.0894 mol
37. For the isomerisation reaction:



$K_p$  equals 25 at 500°C. If the initial pressures of butane and isobutane are 10. atm and 0.0 atm respectively, what are the pressures of the two gases at equilibrium?

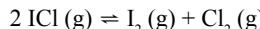
- a.  $P(\text{butane}) = 10 \text{ atm}$  and  
 $P(\text{isobutane}) = 0.40 \text{ atm}$

- b.  $P(\text{butane}) = 9.8 \text{ atm}$  and  
 $P(\text{isobutane}) = 0.38 \text{ atm}$

- c.  $P(\text{butane}) = 0.46 \text{ atm}$  and  
 $P(\text{isobutane}) = 10 \text{ atm}$

- d.  $P(\text{butane}) = 0.38 \text{ atm}$  and  
 $P(\text{isobutane}) = 9.6 \text{ atm}$

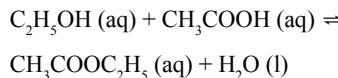
38. At a certain temperature the equilibrium constant ( $K_c$ ) equal 0.11 for the reaction



What is the equilibrium concentration of ICl if 0.75 mol of  $\text{I}_2$  and 0.75 mol of  $\text{Cl}_2$  are initially mixed in a 2.0 litre flask?

- a. 0.45 M
- b. 1.45 M
- c. 0.14 M
- d. 0.90 M

39. The esterification of acetic acid and ethanol is given by the reaction below:



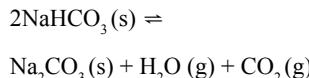
When 1.00 mol of ethanol was mixed with 2.00 mol of acid in a 1.00 litre flask, 0.86 mol of ester was formed at room temperature. What is the value of the equilibrium constant ( $K_c$ )?

- a. 2.8
- b. 5.4
- c. 6.4
- d. 10.8

40.  $K_p$  is equal to 48.70 at 731 K for the reaction:  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ . Initially the mixture contains 0.08592 atm each of  $\text{H}_2$  and  $\text{I}_2$  and 1.0000 atm of  $\text{HI}$ . What is the pressure of  $\text{HI}$  at equilibrium?

- a. 0.9108 atm
- b. 0.8796 atm
- c. 0.1908
- d. 0.02859

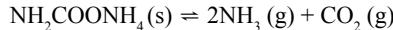
41. When baking soda is heated it decomposes according to the following reaction:



If sufficient baking soda is placed in a container and heated to 90°C, the total pressure of the gases is 0.5451 atm. What is the value of  $K_p$  at the temperature?

- a. 0.05428
- b. 0.18754
- c. 0.4728
- d. 0.07428

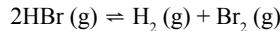
42. Ammonium carbamate can dissociate into gases at 25°C according to the reaction:



If sufficient ammonium carbamate is sealed in a flask, the total pressure will be 0.117 atm at equilibrium. What is the value of  $K_p$  at 25°C?

- a.  $1.47 \times 10^{-3}$
- b.  $2.37 \times 10^{-4}$
- c.  $4.77 \times 10^{-3}$
- d.  $3.58 \times 10^{-4}$

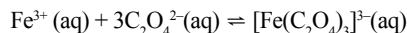
43. Gaseous hydrogen bromide decomposes at elevated temperatures according to the following equation:



At a certain temperature a 2.00 litre flask is initially filled only with 0.600 mol of HBr. What is the value of  $K_c$  at that temperature if the flask contains 0.104 mol of  $\text{H}_2$  at equilibrium?

- a.  $3.04 \times 10^{-2}$
- b.  $6.40 \times 10^{-3}$
- c.  $7.04 \times 10^{-2}$
- d.  $2.24 \times 10^{-2}$

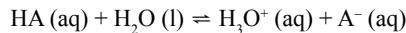
44.  $K_c$  is  $1.67 \times 10^{20}$  at 25°C for the formation of iron(III) oxalate complex ion:



If 0.0100 M  $\text{Fe}^{3+}$  is initially mixed with 1.00 M oxalate ion, what is the concentration of  $\text{Fe}^{3+}$  ion at equilibrium?

- a.  $2.48 \times 10^{-23}$  M
- b.  $6.56 \times 10^{-23}$  M
- c.  $1.67 \times 10^{20}$  M
- d.  $5.68 \times 10^{23}$  M

45. Acids donate protons to water according to the general equation:



Consider the following acids and their equilibrium constants for reaction with water at 25°C. If all the acids have same initial concentration, which is the strongest acid (that is, which donates the most protons to water)?

- a.  $\text{HNO}_3, K_c = 5.4 \times 10^{-4}$
- b.  $\text{HIO}_3, K_c = 1.7 \times 10^{-1}$
- c.  $\text{HBrO}, K_c = 3.7 \times 10^{-3}$
- d.  $\text{HF}, K_c = 2.2 \times 10^{-3}$

46. The solubility of 1:1 salts is measured by the equilibrium constant for the general reaction:  $\text{MX}(\text{s}) = \text{M}^{n+}(\text{aq}) + \text{X}^{n-}(\text{aq})$ . Given the following salts and their equilibrium constants for the reaction above at 25°C, which salt is the least soluble?

- a.  $\text{BaCO}_3, K_c = 3.6 \times 10^{-9}$
- b.  $\text{SrCO}_3, K_c = 5.6 \times 10^{-10}$
- c.  $\text{MgCO}_3, K_c = 6.4 \times 10^{-7}$
- d.  $\text{CaCO}_3, K_c = 4.5 \times 10^{-6}$

47. Which of the following changes in reaction conditions will alter the composition of an equilibrium mixture of gases?

- a. Increasing the temperature
- b. Decreasing the pressure or volume
- c. Addition of reactants or products
- d. All of the above will alter the equilibrium concentrations

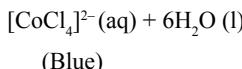
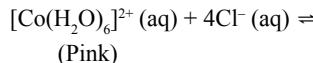
48. Which of the following changes in reactions conditions will not alter the equilibrium concentrations?

- a. Increasing the temperature
- b. Decreasing the pressure or volume
- c. Addition of an inert gas to the reaction mixture
- d. Addition of reactants or products

49. "If a stress is applied to a reaction mixture at equilibrium, the reaction occurs in the direction that will relieve the stress". This statement is called

- a. Law of mass action
- b. Le Chatelier's principle
- c. First law of thermodynamics
- d. Law of combining volumes

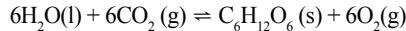
50. The pink and blue species below form a violet coloured mixture at equilibrium:



As the concentration of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is increased, what happens to the solution?

- a. No colour change is observed
- b. The solution becomes colourless
- c. The concentration of  $[\text{CoCl}_4]^{2-}$  decreases
- d. The concentration of  $[\text{CoCl}_4]^{2-}$  increases

51. The overall reaction for photosynthesis can be represented by the following equation

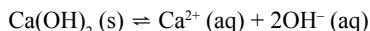


The enthalpy change for this reaction is 2802 kJ. Which of the following changes in condition will shift the equilibrium to the right?

- a. Increase the temperature
- b. Remove one-half of  $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$
- c. Increase the pressure of  $\text{O}_2$
- d. Remove  $\text{CO}_2$  by reaction with  $\text{CaO}(\text{s})$ .

52. The dissolution of calcium hydroxide is exothermic.

## 5.28 ■ Chemical Equilibrium



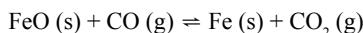
What happens when the solution of  $\text{Ca(OH)}_2$  is heated?

- a. The  $\text{Ca(OH)}_2$  (s) completely dissolves.
  - b. The amount of  $\text{Ca(OH)}_2$  (s) decreases.
  - c. The amount of  $\text{Ca(OH)}_2$  (s) increases.
  - d. The amount of  $\text{Ca(OH)}_2$  (s) remains unchanged.
53. Which change in the system will drive equilibrium to the left in the following reaction?



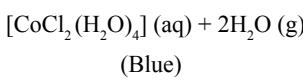
- a. Increase the volume
- b. Increase the pressure
- c. Decrease the amount of  $\text{NO}_3$
- d. Increase the amount of  $\text{N}_2\text{O}_5$

54. Iron oxide ores are reduced to iron metal by exothermic reaction with carbon monoxide.



Which of the following changes in condition will cause the equilibrium to shift to the right?

- a. Add  $\text{CO}_2$
  - b. Add  $\text{FeO}$
  - c. Add CO
  - d. Raise the temperature
55. Ammonium bromide is a crystalline solid that decomposes endothermically when heated:  $\text{NH}_4\text{Br}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HBr}(\text{g})$ . When solid  $\text{NH}_4\text{Br}$  is added to an evacuated flask at  $300^\circ\text{C}$ , which change in reaction conditions below will cause the equilibrium to shift to the right?
- a. Decrease the temperature
  - b. Double the volume of the container
  - c. Add more  $\text{NH}_3$
  - d. Add more  $\text{NH}_4\text{Br}$
56. A crude type of disappearing ink is based on the following endothermic equilibrium:



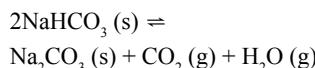
If the reactant solution is used to write on a piece of paper and the paper is allowed to partially dry, what can be done to bring out the coloured handwriting.

- a. Put the paper in the oven
- b. Add water

- c. Put the paper in the freezer

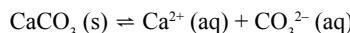
- d. Decrease the volume

57. The enthalpy for the following reaction is 136 kJ. If the reaction takes place in a closed container, which one of the following reaction conditions will not decrease the concentration of water vapour?



- a. Cool the container
- b. Add  $\text{CO}_2$
- c. Remove some  $\text{NaHCO}_3$
- d. Decrease the volume of the container

58. Calcium carbonate is relatively insoluble and the dissolution reaction is endothermic.



Which change in reaction condition below will shift the equilibrium to the right?

- a. Increase the temperature
- b. Add an anion with which  $\text{Ca}^{2+}$  is even more soluble than calcium carbonate
- c. Add an acid to react with  $\text{CO}_3^{2-}$  ion
- d. All of the above will shift reaction to the right.

59. The decomposition of nitrosyl bromide is exothermic:

$2\text{NOBr}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Br}_2(\text{g})$ . Which of the following changes in reaction condition will shift the reaction to the left?

- a. Decrease the temperature
- b. Increase the container volume
- c. Add more  $\text{NOBr}$
- d. None of these

60. Which of the following changes in reaction conditions will not alter the composition of a homogeneous equilibrium mixture of gases?

- a. Increasing the pressure or volume
- b. Decrease the temperature
- c. Addition of reactants or products
- d. Addition of a catalyst

61. Which of the following statements about a catalyst is true?

- a. A catalyst provides a lower energy pathway for a reaction.
- b. A catalyst changes the position of the equilibrium in a reaction

- c. A catalyst increases the temperature of a reaction  
d. A catalyst is consumed in a chemical reaction.
- 62.** A catalyst increases the rate of a chemical reaction by providing a lower energy mechanism for the reaction. When this occurs, which one of the following is not affected?
- Activation energy for the reverse reaction
  - Equilibrium constant
  - Activation energy for the forward reaction
  - Rate of the reverse reaction.
- 63.** A reaction reaches dynamic equilibrium at a given temperature when
- Opposing reactions cease and the system is static.
  - The amount of products exceeds the amount of reactants
  - The relative amounts of reactants and products are constant and rate (forward) = rate (reverse)
  - $k$  (forward) =  $k$  (reverse)
- 64.** At  $25^\circ\text{C}$ , a certain first order reaction has a rate constant equal to  $1.00 \times 10^{-3} \text{ s}^{-1}$  and an equilibrium constant ( $K_c$ ) equal to 4.18. What is the rate constant for the reverse reaction?
- $1.48 \times 10^{-3} \text{ s}^{-1}$
  - $2.39 \times 10^{-4} \text{ s}^{-1}$
  - $4.29 \times 10^{-3} \text{ s}^{-1}$
  - $3.39 \times 10^{-4} \text{ s}^{-1}$
- 65.** Nickel metal can be prepared by the reduction of nickel oxide:
- $$\text{NiO (s)} + \text{CO (g)} \rightleftharpoons \text{CO}_2 (\text{g}) + \text{Ni (s)}$$
- At  $936 \text{ K}$ ,  $K_p = 4.54 \times 10^3$  and at  $1125 \text{ K}$ ,  $K_p = 1.58 \times 10^3$ . Which statement is true?
- The reaction is exothermic
  - The activation energy decreases with increasing temperature.
  - The reaction is endothermic
  - The activation energy increases with increasing temperature.
- 66.** The reaction below virtually goes to completion because cyanide ion forms very stable complexes with  $\text{Ni}^{2+}$  ion:
- $$[\text{Ni}(\text{H}_2\text{O})_6]^{2+} (\text{aq}) + 4 \text{CN}^- (\text{aq}) \rightarrow [\text{Ni}(\text{CN})_4]^{2-} (\text{aq}) + 6\text{H}_2\text{O (l)}$$

At the same time, incorporation of  $^{14}\text{C}$  labeled cyanide ( $^{14}\text{CN}^-$ ) is very rapid:

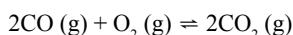
- Which statement below is correct with regard to stability and rate of reaction?
- Unstable species react rapidly
  - Equilibrium is static
  - Stable species can react rapidly
  - Stable species do not react rapidly

### Brainteasers Objective Type Questions (Single choice only)

- 67.** When reaction (1) and (2) below are added together, the result is reaction (3).
- $\text{H}_2\text{O (l)} + \text{HNO}_2 (\text{aq}) \rightleftharpoons \text{H}_3\text{O}^+ (\text{aq}) + \text{NO}_2^- (\text{aq})$
  - $\text{H}_3\text{O}^+ (\text{aq}) + \text{OH}^- (\text{aq}) \rightleftharpoons 2\text{H}_2\text{O (l)}$
  - $\text{HNO}_2 (\text{aq}) + \text{OH}^- (\text{aq}) \rightleftharpoons \text{NO}_2^- (\text{aq}) + \text{H}_2\text{O (l)}$
- If  $K_1 = 4.50 \times 10^{-4}$ , and  $K_2 = 1.00 \times 10^{14}$ , find the equilibrium constant  $K_3$ .
- $2.50 \times 10^{12}$
  - $0.50 \times 10^{10}$
  - $4.50 \times 10^{10}$
  - $3.56 \times 10^8$
- 68.** Find the equilibrium constant for the reaction:  $\text{A (g)} + \text{B (g)} \rightleftharpoons 2\text{C (g)}$  at  $25^\circ\text{C}$  when  $k$  equals  $1.4 \times 10^{-12} \text{ M}^{-1} \text{ s}^{-1}$  for the reaction  $\text{A (g)} + \text{B (g)} \rightarrow 2\text{C (g)}$  at  $25^\circ\text{C}$  and  $k$  equals  $2.7 \times 10^{-13} \text{ M}^{-1} \text{ s}^{-1}$  for the reaction:
- $$2\text{C (g)} \rightarrow \text{A (g)} + \text{B (g)} \text{ at } 25^\circ\text{C}.$$
- 5.2
  - 6.4
  - 3.6
  - 7.1
- 69.** For the reaction:
- $$\text{PCl}_5 (\text{g}) \rightleftharpoons \text{PCl}_3 (\text{g}) + \text{Cl}_2 (\text{g})$$
- the forward reaction at constant temperature is favoured by
- introducing an inert gas at constant volume
  - introducing chlorine gas at constant volume
  - introducing an inert gas at constant pressure
  - increasing the volume of the container
  - introducing  $\text{PCl}_5$  at constant volume.
- I, II, III
  - IV, V
  - II, III, V
  - III, IV, V

## 5.30 ■ Chemical Equilibrium

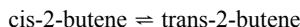
70. An equilibrium mixture of CO, O<sub>2</sub> and CO<sub>2</sub> at a certain temperature contains 0.0010 M CO<sub>2</sub> and 0.0015 M O<sub>2</sub>. At this temperature (K<sub>c</sub>) equals 1.4 × 10<sup>2</sup> for the reaction:



What is the equilibrium concentration of CO?

- a.  $1.1 \times 10^{-3}$  M
- b.  $2.2 \times 10^{-3}$  M
- c.  $4.8 \times 10^{-2}$  M
- d.  $6.6 \times 10^{-6}$  M

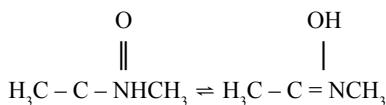
71. The equilibrium constant (K<sub>p</sub>) equals 3.40 for the isomerization reaction:



If a flask initially contains 0.250 atm of cis-2-butene and 0.125 atm of trans-2-butene, what is the equilibrium pressure of each gas?

- a. P (cis-2-butene) = 0.085 atm,  
P (trans-2-butene) = 0.290 atm
- b. P (cis-2-butene) = 0.058 atm,  
P (trans-2-butene) = 0.230 atm
- c. P (cis-2-butene) = 0.028 atm,  
P (trans-2-butene) = 0.156 atm
- d. P (cis-2-butene) = 0.034 atm,  
P (trans-2-butene) = 0.128 atm

72. The following two isomers of C<sub>3</sub>H<sub>7</sub>NO exist in equilibrium with each other in solution:

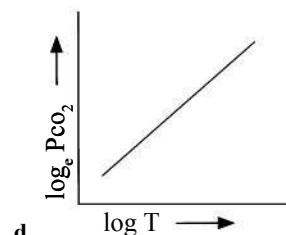
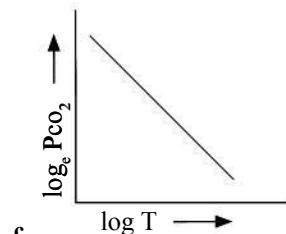
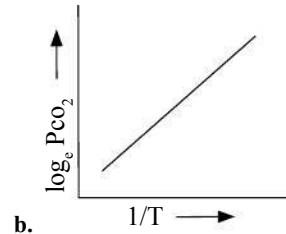
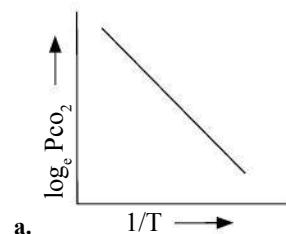


If K<sub>c</sub> = 0.57 at 25°C and the initial concentration of the reactant is 0.50 M and the product is 0.70 M, what are the concentrations at equilibrium?

- a. [Reactant] = 0.46 M and  
[Product] = 0.28 M
- b. [Reactant] = 0.69 M and  
[Product] = 0.48 M
- c. [Reactant] = 0.96 M and  
[Product] = 0.47 M
- d. [Reactant] = 0.76 M and  
[Product] = 0.44 M

73. For the chemical equilibrium,
- $$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$

$\Delta H_f^\circ$  can be determined from which one of the following plots?



74. Phosphorous pentachloride decomposes to phosphorous trichloride at high temperatures according to the reaction:

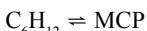


At 250°C, 0.250 M PCl<sub>5</sub> is added to a flask. If K<sub>c</sub> = 1.80, What are the equilibrium concentrations of each gas?

- a. [PCl<sub>5</sub>] = 2.26 M, [PCl<sub>3</sub>] = 2.04 M, [Cl<sub>2</sub>] = 20.4 M
- b. [PCl<sub>5</sub>] = 0.0280 M, [PCl<sub>3</sub>] = 0.222 M, [Cl<sub>2</sub>] = 0.222 M
- c. [PCl<sub>5</sub>] = 1.28 M, [PCl<sub>3</sub>] = 1.028 M, [Cl<sub>2</sub>] = 1.028 M

- d.  $[PCl_5] = 3.82 \text{ M}$ ,  $[PCl_3] = 0.879 \text{ M}$ ,  
 $[Cl_2] = 20.4 \text{ M}$

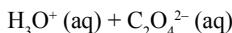
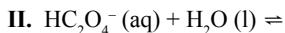
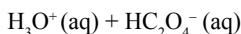
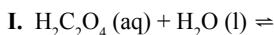
75. Cyclohexane ( $C_6H_{12}$ ) undergoes a molecular rearrangement in the presence of  $AlCl_3$  to form methylcyclopentane (MCP) according to the equation:



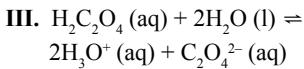
If  $K_c = 0.143$  at  $25^\circ\text{C}$  for this reaction, predict the direction the reaction will shift, if the initial concentrations of  $C_6H_{12}$  and MCP are  $0.200 \text{ M}$  and  $0.100 \text{ M}$ , respectively. The system

- a. is already at equilibrium
- b. will shift right
- c. will shift left
- d. is not at equilibrium and will remain in an unequilibrated state.

76. Oxalic acid can donate two protons to water in successive reactions:

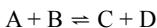


If  $K_{C_1} = 5.9 \times 10^{-2}$  and  $K_{C_2} = 6.4 \times 10^{-5}$  at  $25^\circ\text{C}$ , what is the value of  $K_c$  for reaction (3)?



- a.  $7.6 \times 10^{-4}$
- b.  $5.8 \times 10^{-3}$
- c.  $6.4 \times 10^{-5}$
- d.  $3.8 \times 10^{-6}$

77. The equilibrium constant for gaseous reaction:



is 100 at  $25^\circ\text{C}$ . Consider the following statements in this regard. If the initial concentration of all the four species were  $1.0 \text{ M}$  each, then the equilibrium concentration of

- I. A would be  $0.182 \text{ mol/L}$
- II. C would be  $0.818 \text{ mol/L}$
- III. D would be  $1.818 \text{ mol/L}$

Of these statements:

- a. I and III are correct
- b. I and II are correct
- c. II and III are correct
- d. I, II and III are correct

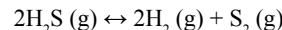
78. What is the equilibrium constant ( $K_c$ ) for the reaction:

$2Hg \text{ (l)} + O_2 \text{ (g)} \rightleftharpoons 2HgO \text{ (s)}$  if the amounts of reactants and products at equilibrium are  $1.00 \text{ g}$  of

$HgO \text{ (s)}$ ,  $2.00 \text{ ml}$  of  $Hg \text{ (l)}$ , and  $1.60 \text{ M } O_2 \text{ (s)}$ ? (The molar mass and density of  $HgO \text{ (s)}$  is  $217 \text{ g/mol}$  and  $1.10 \text{ g/cm}^3$ . The molar mass and density of  $Hg \text{ (l)}$  is  $201 \text{ g/mol}$  and  $13.6 \text{ g/ml}$ ).

- a.  $0.625$
- b.  $1.625$
- c.  $6.25 \times 10^{-3}$
- d.  $1.28 \times 10^3$

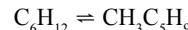
79. An equilibrium mixture for the reaction



had 1 mole of  $H_2S$ , 0.2 mole of  $H_2$  and 0.8 mole of  $S_2$  in a 2 litre flask. The value of  $K_c$  in  $\text{mol L}^{-1}$  is

- a.  $0.08$
- b.  $0.016$
- c.  $0.004$
- d.  $0.160$

80. Cyclohexane ( $C_6H_{12}$ ) undergoes a molecular rearrangement in the presence of  $AlCl_3$  to form methylcyclopentane ( $CH_3C_5H_9$ ), according to the equation



If  $K_c = 0.143$  at  $25^\circ\text{C}$  for this reaction, find the equilibrium concentrations of  $C_6H_{12}$  and  $CH_3C_5H_9$  if the initial concentrations are  $0.200 \text{ M}$  and  $0.100 \text{ M}$  respectively

- a.  $[C_6H_{12}] = 0.286 \text{ and}$   
 $[CH_3C_5H_9] = 0.016 \text{ M}$
- b.  $[C_6H_{12}] = 0.262 \text{ and}$   
 $[CH_3C_5H_9] = 0.038 \text{ M}$
- c.  $[C_6H_{12}] = 0.186 \text{ and}$   
 $[CH_3C_5H_9] = 0.162 \text{ M}$
- d.  $[C_6H_{12}] = 0.164 \text{ and}$   
 $[CH_3C_5H_9] = 0.621 \text{ M}$

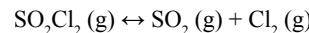
81. What is the correct sequence of active masses in increasing order in gaseous mixture containing one gram per litre of each of the following?

- |                   |                  |
|-------------------|------------------|
| <b>I.</b> $NH_3$  | <b>II.</b> $N_2$ |
| <b>III.</b> $H_2$ | <b>IV.</b> $O_2$ |

Select the correct answer using the codes given below:

- a. III, I, IV, II
- b. III, IV, II, I
- c. II, I, IV, III
- d. IV, II, I, III

82. The equilibrium



is attained at  $25^\circ\text{C}$  in a closed container and inert gas helium is introduced. Which of the following statement(s) is/are correct?

- I. concentrations of  $SO_2$ ,  $Cl_2$  and  $SO_2Cl_2$  change
- II. more chlorine is formed

## 5.32 ■ Chemical Equilibrium

III. concentration of  $\text{SO}_2$  is reduced

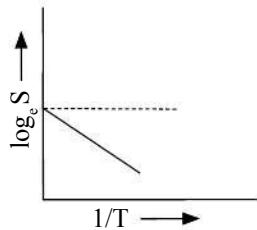
IV. more  $\text{SO}_2\text{Cl}_2$  is formed

- a. I, II, III
- b. II, III, IV
- c. III, IV
- d. none

83. One mole of  $\text{N}_2\text{O}_4$  (g) at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of  $\text{N}_2\text{O}_4$  (g) decomposes to  $\text{NO}_2$  (g). The resultant pressure is
- a. 1.2 atm
  - b. 2.4 atm
  - c. 2.0 atm
  - d. 1.0 atm

84. The solubility of a solute in water varies with temperature and given as  $S = Ae^{-\Delta H/RT}$

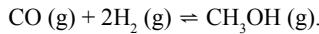
Here  $\Delta H$  is enthalpy of the solution. For the given solute, variation of  $\log_e S$  with temperature can be shown by the figure given below



This solute may be

- a.  $\text{CaSO}_4$
- b.  $\text{CuSO}_4$
- c.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
- d.  $\text{ZnO}$

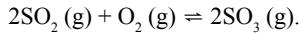
85. A mixture of carbon monoxide, hydrogen and methanol is at equilibrium. The balanced chemical equation is



At 250°C, the mixture contains 0.0960 M CO, 0.191 M  $\text{H}_2$ , and 0.150 M  $\text{CH}_3\text{OH}$ . What is the value for  $K_c$ ?

- a. 4.52
- b. 42.8
- c. 52.9
- d. 0.581

86. The oxidation of sulphur dioxide by oxygen to sulphur trioxide has been implicated as an important step in the formation of acid rain:

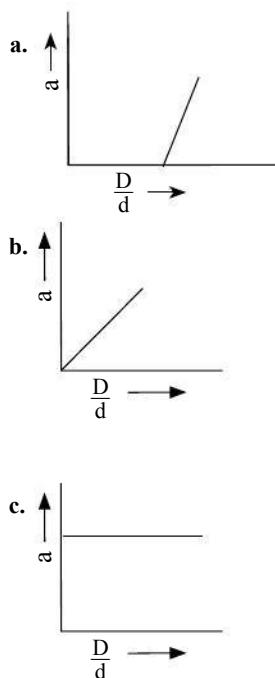


If the equilibrium partial pressures of  $\text{SO}_2$ ,  $\text{O}_2$  and  $\text{SO}_3$  are 0.564 atm, 0.102 atm, and 0.333 atm respectively at 1000 K, what is the  $K_p$  at that temperature?

- a. 2.24
- b. 4.68
- c. 3.42
- d. 13.42

87. For the dissociation of  $\text{PCl}_5$  into  $\text{PCl}_3$  and  $\text{Cl}_2$  in gaseous phase reaction, if  $d$  is the observed vapour density and  $D$  the theoretical vapour density with

'a' as degree of dissociation. Variation of  $D/d$  with 'a' is given by which graph?



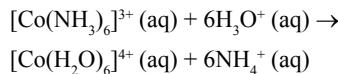
- a. None of these

88. What is the value for  $K_{eq}$  for the following reaction:

$\text{PbCl}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$ , if  $\text{PbCl}_2(\text{s}) = 1.50 \text{ g}$ ,  $[\text{Pb}^{2+}] = 1.6 \times 10^{-2} \text{ M}$  and  $[\text{Cl}^-] = 3.2 \times 10^{-2} \text{ M}$  at equilibrium? (The molar mass of  $\text{PbCl}_2(\text{s})$  is 278 g/mol and its density is 5.85 g/cm<sup>3</sup>).

- a.  $2.6 \times 10^{-6}$
- b.  $0.8 \times 10^{-6}$
- c.  $1.6 \times 10^{-5}$
- d.  $6.4 \times 10^{-4}$

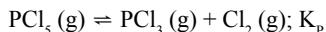
89. The hexaammine cobalt (III) ion is very unstable in acidic aqueous solution:



However, solutions of hexaammine cobalt(III) can be stored in acidic solution for months without noticeable decomposition. Which statement below about the equilibrium constant and the activation energy for the reaction is true?

- a.  $K_{eq} > 10^3$  and  $E_a$  is very large
- b.  $K_{eq} < 10^3$  and  $E_a$  is very small
- c.  $K_{eq} < 10^3$  and  $E_a$  is very large
- d.  $K_{eq} > 10^3$  and  $E_a$  is very small

90. For the decomposition of  $\text{PCl}_5(\text{g})$  in a closed vessel, the degree of dissociation is  $\alpha$  at total pressure ( $P$ ).

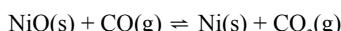


Which among the following relations is correct?

- a.  $\alpha = \sqrt{[(K_p + P)/K_p]}$
  - b.  $\alpha = \sqrt{[K_p/(K_p + P)]}$
  - c.  $\alpha = 1/\sqrt{[K_p + P]}$
  - d.  $\alpha = \sqrt{[K_p + P]}$
91. The equilibrium constant  $K_c$  for the reaction  $\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$  at a particular temperature is  $6.0 \times 10^{-5}$ . The ratio of the concentration of  $\text{NO}_2$  to  $\text{O}_2$  at equilibrium is 0.0152. The equilibrium concentration of  $\text{N}_2$  is

- a. 0.253 mol/litre
- b.  $3.85 \times 10^2$  mol/litre
- c. 3.85 mol/litre
- d.  $2.53 \times 10^2$  mol/litre

92.  $\text{NiO}$  is to be reduced to nickel metal in an industrial process by use of the reaction.



At 1600 K the equilibrium constant for the reaction is  $K_p = 6.0 \times 10^2$ . If a CO pressure of 150 torr is

to be employed in the furnace and total pressure never exceeds 760 torr, will reduction occur?

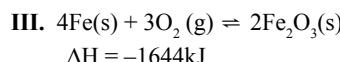
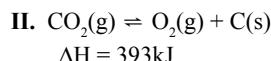
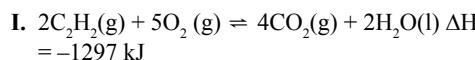
- a. No
- b. Yes
- c. Cannot be said
- d. May or may not

93. For the reaction

$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ ,  $\Delta H = -93.6 \text{ kJ mol}^{-1}$ , the concentration of  $\text{H}_2$  at equilibrium can be increased by

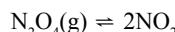
- I. lowering the temperature
  - II. increasing the volume of the system
  - III. adding  $\text{N}_2$  at constant volume
  - IV. adding  $\text{H}_2$  at constant volume
- a. II, IV
  - b. only II is correct
  - c. I, II and III are correct
  - d. III and IV are correct
  - e. only IV is correct

94. Which of the following reactions, initially at equilibrium, will shift to the left when the temperature is decreased at constant pressure?

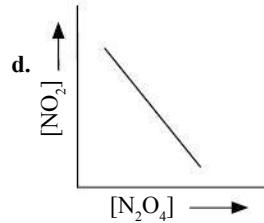
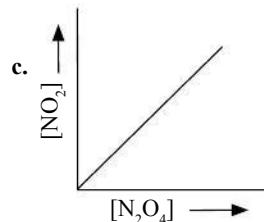
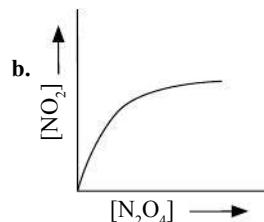
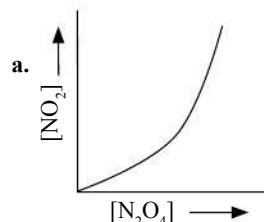


- a. (i)
- b. (ii)
- c. (iii)
- d. all of them

95. The graph which represents all the equilibrium concentrations for the reaction



(the concentrations of  $\text{N}_2\text{O}_4(\text{g})$  and of  $\text{NO}_2(\text{g})$  for which the following reation will be at equilibrium will lie on which of the following graph)



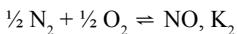
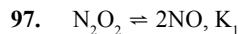
96.  $K_c = 0.0112$  at  $25^\circ\text{C}$  for the reaction  $\text{N}_2(\text{g}) + \text{O}_2 \rightleftharpoons 2\text{NO}(\text{g})$

What the change in the state of the reaction occurs (if any) if  $[\text{N}_2]_0 = 2.00\text{M}$ ,  $[\text{O}_2]_0 = 0.500\text{M}$ ?

## 5.34 ■ Chemical Equilibrium

- a. Reaction produces more NO,  $Q < K_c$ .
- b. No change occurs in concentrations,  $Q = K_c$ .
- c. Temperature increases.
- d. Reaction produces more reactants,  $Q > K_c$

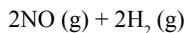
### Multiple Correct Answer Type Questions



Correct relation between  $K_1, K_2, K_3$  and  $K_4$  is/are

- a.  $\sqrt{(K_1 \times K_4)} = 1$
- b.  $K_1 \times K_3 = 1$
- c.  $\sqrt{(K_1 \times K_2)} = 1$
- d.  $\sqrt{K_3 \times K_2} = 1$

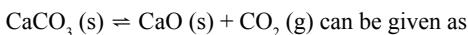
98. The following reaction attains equilibrium at high temperature



The amount of NO is affected by

- a. Addition of catalyst
- b. Compressing the reaction mixture
- c. Increasing the nitrogen concentration
- d. Decreasing the hydrogen concentration

99. The equilibrium constant for the reaction



- a.  $K_C = ([CaO][CO_2])/[CaCO_3]$
- b.  $K_C = [CO_2]$
- c.  $K_p = P_{CO_2}$
- d.  $K_C = [CaCO_3]/([CaO][CO_2])$

100. Which of the following does not affect the value of equilibrium constant of a reaction?

- a. Change in temperature
- b. Addition of a catalyst
- c. Change in the concentration of the reactants
- d. Change in pressure

101. Which of the following statement is/are incorrect here?

- a. Equilibrium constant of an exothermic reaction decreases with the increase of temperature
- b.  $K_p$  is always greater than  $K_c$

- c. At equilibrium, concentrations of reactants and products become constant as the reaction stops
- d. Addition of a catalyst speeds up the forward reaction more than the backward reaction

102. For the reaction



the forward reaction at constant temperature is favoured by

- a. Increasing the volume of the container
- b. Introducing  $PCl_5$  at constant volume
- c. Introducing an inert gas at constant volume
- d. Introducing  $Cl_2(g)$  at constant volume

103. When  $NaNO_3$  is heated in a closed vessel oxygen is liberated and  $NaNO_2$  is left behind. At equilibrium, which are not correct?

- a. Increase of pressure favours reverse reaction
- b. Increase of temperature favours forward reaction
- c. Addition of  $NaNO_2$  favours reverse reaction
- d. Addition of  $NaNO_3$  favours forward reaction

104. Which of the following statement (s) is/are correct:

- a. A plot of  $P$  vs  $1/V$  is linear at constant temperature
- b. A plot of  $\log_{10} K_p$  vs  $1/T$  is linear
- c. A plot of  $\log [X]$  vs time is linear for a first order reaction,  $X \rightarrow P$
- d. A plot of  $\log_{10} P$  vs  $1/T$  is linear at constant volume

105. Which of the following have  $K_p = K_c$  here?

- a.  $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$
- b.  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH(g)$
- c.  $H_2(g) + X_2(g) \rightleftharpoons 2HX(g)$
- d.  $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

106. Which of the following statement is/are correct about the equilibrium?

- a.  $\Delta G = 0$
- b. Catalyst has no effect on equilibrium
- c.  $K_{eq}$  changes with temperature
- d. Value of  $K_{eq}$  changes by increasing concentration of equilibrium

107. Which of the following reaction can have same units of  $K_p$ ?

- a.  $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$
- b.  $2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$
- c.  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}(\text{g})$
- d.  $\text{XX}_2(\text{g}) \rightleftharpoons \text{XY}(\text{g}) + \text{Y}(\text{g})$

108. The degree of dissociation ( $\alpha$ )

$$\alpha = \frac{D - d}{(n - 1)d}$$

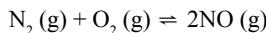
Incorrect match for the equilibrium

- a.  $P = \frac{4n}{5}Q + \frac{n}{2}R$
- b.  $P = \frac{n}{3}Q + \frac{2n}{3}R$
- c.  $P = \frac{5n}{6}Q + \frac{n}{6}R$
- d.  $P = \frac{n}{2}Q + \frac{n}{2}R$

109. Which of the following statement is/are correct for a reversible reaction?

- a. At a given temperature both  $Q$  and  $K$  vary with the progress of the reaction.
- b. When  $Q > K$ , the reaction proceeds in backward direction before coming to stand still.
- c. Reaction quotient ( $Q$ ) is the ratio of the product or arbitrary molar concentrations of the products to those of the reactants.
- d.  $Q$  may be  $<>= K$ .

110. Which of the following factors will not disturb the equilibrium state of this reaction?



- a. Change in temperature
- b. Change in pressure
- c. Addition of  $\text{N}_2$
- d. Addition of a catalyst

111. For the gas phase reaction,

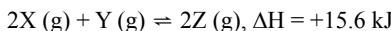
$\text{C}_2\text{H}_4 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6$  ( $\Delta H = -32.7$  kcal), carried out in a closed vessel, the equilibrium concentration of  $\text{C}_2\text{H}_4$  can be increased by

- a. Decreasing the pressure
- b. Adding some  $\text{C}_2\text{H}_6$
- c. Increasing the temperature
- d. Removing some  $\text{H}_2$

112. If the volume of the reaction flask is reduced to half of its initial value and temperature is kept constant then in which of the following cases the position of the equilibrium will shift?

- a.  $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$
- b.  $\text{I}_2(\text{g}) \rightleftharpoons 2\text{I}(\text{g})$
- c.  $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{s})$
- d.  $2\text{NOCl}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g})$

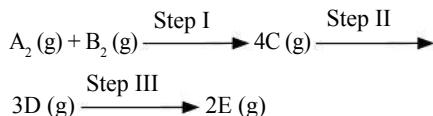
113. For the reaction,



Which of the following will increase the extent of the reaction at equilibrium?

- a. Addition of catalyst
- b. Increasing concentration of  $\text{Z}$
- c. Increasing the temperature
- d. Increasing the pressure

114. In this three step endothermic reaction



Which of the following statement is/are correct?

- a. Step III is favoured by low temperature and high pressure
- b. Step I is favoured by high temperature and low pressure
- c. Step II is favoured by high temperature and high pressure
- d. Step III is favoured by high temperature and low pressure

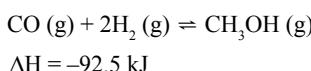
115. For which of the following reactions,  $K_p/K_c = RT$ ?

- a.  $2\text{HX}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{X}_2(\text{g})$
- b.  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
- c.  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
- d.  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

116. Which of the following are homogeneous equilibria?

- a.  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
- b.  $\text{H}_2(\text{g}) + \text{X}_2(\text{g}) \rightleftharpoons 2\text{HX}(\text{g})$
- c.  $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$
- d.  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

117. Consider the following reversible reaction:



## 5.36 ■ Chemical Equilibrium

Which factor(s) will increase the yield of methanol at equilibrium?

- a. Addition of inert gas at constant volume
- b. Increased pressure on the system
- c. Increased temperature
- d. Increased partial pressure of hydrogen

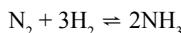
118. The variation of equilibrium constant K with temperature is represented by

- a.  $\log_e K_2 - \log_e K_1 = -\frac{\Delta H}{R} \int_{T_1}^{T_2} d(1/T)$
- b.  $[(d \log_e K)/dT]_p = -\frac{\Delta H}{RT}$
- c.  $\log_e K = \text{constant} - \frac{RT}{\Delta H}$
- d.  $\log_e K = \text{constant} - \frac{\Delta H}{RT}$

119. The reactions in which the yield of the products can not be increased by the applications of high pressure is/are

- a.  $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
- b.  $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$
- c.  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
- d.  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ .

120. An inert gas is added to the reaction



at constant volume. Which of the following is/are incorrect?

- a. Backward reaction is favoured
- b. The reaction remains unaffected
- c. The reaction ceases to proceed
- d. Forward reaction is favoured

121. Which of the following is/are correct?

- a. The equilibrium constant does not depend upon pressure
- b. When pressure is applied on ice  $\Rightarrow$  water equilibrium more water will be formed
- c. The equilibrium constant increases when a catalyst is introduced
- d. Changes with temperature

## Linked-Comprehension Type Questions

### Comprehension 1

The decomposition of  $NH_4HS(s)$  takes place as follows:



If we take 3.06 gm of solid  $NH_4HS$  into a two litre evacuated vessel at 300 K. It undergoes 30% decomposition.

122. For this decomposition the value of  $K_c$  is?

- a.  $16.2 \times 10^{-5} \text{ mol}^2 \text{ lit}^{-2}$
- b.  $8.1 \times 10^{-5} \text{ mol}^2 \text{ lit}^{-2}$
- c.  $4.05 \times 10^{-5} \text{ mol}^2 \text{ lit}^{-2}$
- d.  $1.62 \times 10^{-3} \text{ mol}^2 \text{ lit}^{-1}$

123. The value of  $K_p$  is

- a.  $0.0245 \text{ atm}^2$
- b.  $0.049 \text{ atm}^2$
- c.  $8.1 \times 10^{-5} \text{ atm}^2$
- d.  $0.081 \text{ atm}^2$

124. What will be the effect of adding more amount of  $NH_4HS$  on equilibrium?

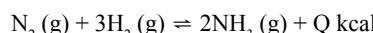
- a. Equilibrium will shift in forward direction
- b. Equilibrium will shift in backward direction
- c. Equilibrium remains unaffected
- d. Equilibrium first shifts in forward direction and then becomes constant

125. Which relation is correct here?

- a.  $K_p = K_c$
- b.  $K_p < K_c$
- c.  $K_p = K_c$
- d. Can't be predicted here

### Comprehension 2

The dynamic nature of chemical equilibrium can be easily demonstrated by in the synthesis of ammonia by Haber's method.



Haber took definite amount of  $N_2$  and  $H_2$  at suitable conditions of temperature and pressure. He was able to find amount of  $NH_3$  and unreacted amount of  $H_2$ ,  $N_2$  at various time intervals.

126. Which of the following condition is not favourable for formation of more ammonia in this process

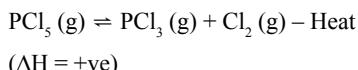
- I. Higher temperature
  - II. More pressure
  - III. More concentration of  $\text{NH}_3$
  - IV. More concentration of  $\text{N}_2$  and  $\text{H}_2$
- a. I, II, III      b. I, III  
c. II, III, IV      d. I, III, IV

127. If the value of  $K_p$  for this reaction at 673 K is found to be  $16.4 \times 10^{-3}$  then the value of  $\Delta G^\circ$  is
- a. 11.733 kcal  
b. 11.733 cal  
c. 931.6 kcal  
d. 9.316 cal
128. If at a temperature the value of  $K_c$  for the reaction  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  is  $1.49 \times 10^{-5} \text{ mol}^{-2} \text{ lit}^2$ . What will be the value of  $K_c'$  for  $\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \rightleftharpoons 2\text{NH}_3$ ?
- a.  $1.49 \times 10^{-5} \text{ lit/mol}$   
b.  $3.86 \times 10^{-3} \text{ lit mol}^{-1}$   
c.  $3.86 \times 10^{-3} \text{ lit}^2 \text{ mol}^{-2}$   
d.  $1/\sqrt{(1.49 \times 10^{-5}) \text{ lit}^{-2} \text{ mol}^2}$

129. If the initial molar concentrations of  $\text{N}_2\text{H}_2$  and  $\text{NH}_3$  at 400°C are 0.142 M and 0.0265 M and 0.0384 M respectively predict which statements are correct here?
- I. Here  $Q > K_c$
  - II. The reactants are favoured
  - III. Here  $Q < K_c$
  - IV. Product is favoured
- a. I and III      b. II and III  
c. I and II      d. III and IV

### Comprehension 3

$\text{PCl}_5$  when heated in a sealed tube at 523 K undergoes decomposition as follows:



At this temperature its vapour density is found to be 57.92.

130. For the decomposition of  $\text{PCl}_5(\text{g})$  in a closed vessel which is the correct relation between total

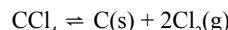
pressure (P), equilibrium constant ( $K_p$ ) and degree of dissociation ( $\alpha$ )

- a.  $\alpha = \sqrt{K_p + P}$   
b.  $\alpha = \sqrt{[1/(K_p + P)]}$   
c.  $\alpha = \sqrt{[K_p/(K_p + P)]}$   
d.  $\alpha = \sqrt{[(K_p + P)/K_p]}$

131. At this temperature when vapour density is 57.92. Find the degree of dissociation of  $\text{PCl}_5$ .
- a. 72%      b. 80%  
c. 88%      d. 40%
132. Find the volume percent of  $\text{Cl}_2$  at equilibrium in  $\text{PCl}_5$  under a total pressure of 1.5 atmosphere. [ $K_p = 0.202$ ]
- a. 12.8%      b. 37.2%  
c. 25.6%      d. 1.28 %
133. The dissociation of  $\text{PCl}_5$  is favoured by
- I. Increase of pressure
  - II. Decrease of pressure
  - III. Increase of temperature
  - IV. More concentration of  $\text{PCl}_5$
- a. I, III, IV      b. II, III, IV  
c. I, IV      d. III and IV

### Comprehension 4

At 700K the equilibrium constant for the reaction



is  $K_p = 0.76$ . A flask is charged with 2.00 atm of  $\text{CCl}_4$ , which then reaches equilibrium at 700 K. 6

134. What is the value of  $K_c$  for this reaction at 700 K?
- a. 1.30      b. 0.013  
c. 0.026      d. 2.6
135. What fraction of the  $\text{CCl}_4$  is converted into C and  $\text{Cl}_2$ ?
- a. 62%      b. 25%  
c. 26%      d. 60%
136. What are the partial pressures of  $\text{CCl}_4$  and  $\text{Cl}_2$  at equilibrium?
- a. 1.47      b. 14.7  
c. 0.147      d. 147.0

### Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given. Mark

- a. If A and R both are correct and R is the correct explanation of A;
  - b. If A and R both are correct but R is not the correct explanation of A;
  - c. A is true but R is false;
  - d. A is false but R is true,
137. (A): For a reaction at equilibrium, the free energy for the reaction is minimum.  
(R): The free energy for both reactants and products decreases and become equal.
138. (A): The endothermic reactions are favoured at lower temperature and the exothermic reactions are favoured at higher temperature.  
(R): When a system in equilibrium is disturbed by changing the temperature, it will tend to adjust itself so as to overcome the effect of change.
139. (A): The reaction  

$$2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2\text{NO}_2$$
is favoured in the forward direction with increase of pressure .  
(R): The reaction is exothermic
140. (A): Concentration of the reactant and product does not change with time at equilibrium for a chemical reaction.  
(R): The rate of a reaction is zero at equilibrium.
141. (A): In the Haber process,  

$$\text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3$$
Pressure is about 200 atm in presence of catalyst and temperature is kept 500°C even the reaction is exothermic.  
(R): Energy needed for this reaction is easily obtained at this temperature.
142. (A): When  $\text{CaCO}_3(\text{s})$  is heated, the loss of  $\text{CO}_2(\text{g})$  from the system causes the reaction to go almost to completion to leave a residue of  $\text{CaO}(\text{s})$ .  
(R): Heating causes gas particles to move with more energy.

143. (A): When the following equilibrium is studied in a vessel of twice the volume of the earlier one,  

$$\text{A}(\text{g}) \leftrightarrow \text{B}(\text{g}) + \text{C}(\text{g})$$
equilibrium constant is decreased.  
(R): Equilibrium constant  

$$K_c = \frac{x^2}{(1-x)V}$$
144. (A): For the reaction  $\text{A} + \text{B} \leftrightarrow \text{C}$ ,  $K_c = 2$ . If we start with 1 mol each of A, B, and C in 5 L flask, then at equilibrium, molar concentration of A and B decreases and that of C increases.  
(R): Reaction quotient  $Q > K_c$  with given quantity of A, B, and C hence reaction is reversed.
145. (A): The equilibrium constant for a reaction having positive  $\Delta H^\circ$  increases with increase of temperature.  
(R): The temperature dependence of the equilibrium constant is related to  $\Delta H^\circ$  and not  $\Delta S^\circ$  for the reaction.
146. (A): The value of K gives us a relative idea about the extent to which a reaction proceeds.  
(R): The value of K is independent of the stoichiometry of reactants and products at the point of equilibrium.
147. (A): On opening a sealed soda bottle dissolved carbon dioxide gas escapes.  
(R): Gas escapes to each the new equilibrium condition of lower pressure.
148. (A): The equilibrium constant is fixed and a characteristic for any given chemical reaction at a specified temperature.  
(R): The composition of the final equilibrium mixture at a particular temperature depends upon the starting amount of reactants.
149. (A): Ice melts slowly at higher altitudes.  
(R): The melting of ice is favoured at high pressure because ice  $\rightarrow$  water shows decrease in volume.
150. (A): When  $Q = K_c$ , reaction is at equilibrium  
(R): At equilibrium  $\Delta G$  is 0.
151. (A): Dissociation of  $\text{PCl}_5$  decreases in presence of  $\text{Cl}_2$   
(R): An increase in concentration of  $\text{Cl}_2$  favours backward reaction to decrease dissociation of  $\text{PCl}_5$

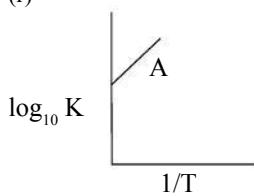
- 152.** (A): Water boils at high temperature in pressure cooker  
 (R) Inside the pressure cooker pressure is less than 1 atm.
- 153.** (A): Some hydrated salts like blue vitriol dissolve in water with absorption of heat  
 (R) Le Chatelliers principle is not valid for solid–solid heterogeneous systems.
- 154.** (A): For every chemical reaction at equilibrium standard Gibbs energy of reaction is zero.  
 (R): At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.

*IIT 2008J*

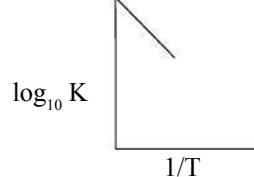
### Matrix-Match Type Questions

- 155.** Match the following:

Column I	Column II
A. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(p) Increase of pressure favours forward reaction
B. $N_2(g) + O_2(g) \rightarrow 2NO(g)$	(q) Constant pressure favours forward reaction
C. $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$	(r)



D.  $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$



(t) Decrease in pressure favours forward reaction

- 156.** Match the following:

Column I	Column II
(A) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	(p) No effect of catalyst on $K_{eq}$

- (B)  $N_2 + O_2 \rightarrow 2NO(g)$  (q) No effect of pressure  
 (C)  $P + Q \rightarrow 2R + S$   $\Delta H = \text{Positive}$  (r)  $K_{eq}$  increases with rise in temperature  
 (D)  $PCl_5 \rightarrow PCl_3 + Cl_2$  (s)  $K_{eq}$  decreases with rise in temperature

- 157.** Match the following:

Column I	Column II
A. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(p) $K_p < K_c$
B. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(q) $K_p$ does not define
C. $2SO_3 \rightleftharpoons 2SO_2 + O_2$	(r) $\Delta n > 0$
D. $CH_3COOC_2H_5(l) + H_2O(l) \rightleftharpoons CH_3COOH(l) + C_2H_5OH(l)$	(s) $K_p > K_c$
	(t) $P_{\text{initial}} > P_{\text{eq}}$

- 158.** Match the following:

Column I	Column II
A. Law of mass action	(p) Guldberg wage
B. Active mass of $CaCO_3(s)$	(q) $K_p = K_c(RT)$ (s)
C. $2SO_2 + O_2 \rightarrow 2SO_3$	(r) 1
D. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$	(s) zero
	(t) $K_p = K_c(RT)^{-1}$

- 159.** Match the following:

Column I	Column II
A. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(l)$	(p) heterogeneous reversible reaction
B. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	(q) $2HI \rightarrow H_2(g) + I_2(g)$
C. $K_p = K_c$	(r) equilibrium state
D. rate of forward reaction = rate of backward	(s) homogeneous reversible reaction

- 160.** Match the following:

Column I (Process)	Column II (Favourable conditions)
A. Melting of ice	(p) High pressure
B. Vaporization of water	(q) High temperature

## 5.40 ■ Chemical Equilibrium

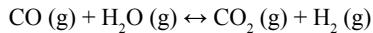
- C. Formation of nitric (r) More concentration of oxide N<sub>2</sub>
- D. Formation of NH<sub>3</sub> by Haber's method (s) Presence of inert gases
- (t) No change in pressure

161. Match the following:

Column I	Column II
A. N <sub>2</sub> (g) + O <sub>2</sub> (g) ⇌ 2NO (g)	(p) K <sub>p</sub> > K <sub>c</sub>
B. 2SO <sub>2</sub> (g) + O <sub>2</sub> (g) ⇌ 2SO <sub>3</sub> (g)	(q) K <sub>p</sub> = K <sub>c</sub>
C. PCl <sub>5</sub> (g) ⇌ PCl <sub>3</sub> (g) + Cl <sub>2</sub> (g)	(r) K <sub>p</sub> < K <sub>c</sub>
D. 2KClO <sub>3</sub> 2KCl + 3O <sub>2</sub>	(s) High temperature (t) Irreversible reaction

### The IIT-JEE Corner

162. For the reaction



at a given temperature, the equilibrium amount of CO<sub>2</sub> (g) can be increased by

- a. adding a suitable catalyst
- b. adding an inert gas
- c. decreasing the volume of the container
- d. increasing the amount of CO (g)

[IIT 1998]

163. For the chemical reaction

3X (g) + Y (g) ⇌ X<sub>3</sub>Y (g), the amount of X<sub>3</sub>Y at equilibrium is affected by

- a. temperature and pressure
- b. temperature only
- c. pressure only
- d. temperature, pressure and catalyst

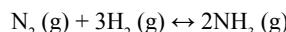
[IIT 1999]

164. When two reactants A and B are mixed to give products C and D, the reaction quotient, Q, at the initial stages of the reaction

- a. is zero
- b. decreases with time
- c. is independent of time
- d. increases with time.

[IIT 2000]

165. For the reversible reaction,



At 500°C, the value of K<sub>p</sub> is  $1.44 \times 10^{-5}$  when partial pressure is measured in atmospheres. The corresponding value of K<sub>c</sub>, with concentration in mole litre<sup>-1</sup>, is

- a.  $1.44 \times 10^{-5}/(0.082 \times 500)^{-2}$
- b.  $1.44 \times 10^{-5}/(8.314 \times 773)^{-2}$
- c.  $1.44 \times 10^{-5}/(0.082 \times 773)^2$
- d.  $1.44 \times 10^{-5}/(0.082 \times 773)^{-2}$

[IIT 2000]

166. At constant temperature, the equilibrium constant (K<sub>p</sub>) for the decomposition reaction N<sub>2</sub>O<sub>4</sub> ⇌ 2NO<sub>2</sub> is expressed by

K<sub>p</sub> =  $(4x^2P)/(1 - x^2)$ , where P = pressure, x = extent of decomposition. Which one of the following statements is true?

- a. K<sub>p</sub> increases with increase of P
- b. K<sub>p</sub> increases with increase of x
- c. K<sub>p</sub> increases with decrease of x
- d. K<sub>p</sub> remains constant with change in P and x.

[IIT 2001]

167. Consider the following equilibrium in a closed container: N<sub>2</sub>O<sub>4</sub> (g) ⇌ 2NO<sub>2</sub> (g). At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant (K<sub>p</sub>) and degree of dissociation ( $\alpha$ )?

- a. neither K<sub>p</sub> nor  $\alpha$  changes
- b. both K<sub>p</sub> and  $\alpha$  change
- c. K<sub>p</sub> changes but  $\alpha$  does not change
- d. K<sub>p</sub> does not change but  $\alpha$  changes.

[IIT 2002]

168. N<sub>2</sub> + 3H<sub>2</sub> ⇌ 2NH<sub>3</sub>

Which is correct statement if N<sub>2</sub> is added at equilibrium condition?

- a. The equilibrium will shift to forward direction because according to 2nd law of thermodynamics the entropy must increase in the direction of spontaneous reaction
- b. The condition for equilibrium is GN<sub>2</sub> + 3GH<sub>2</sub> = 2GNH<sub>3</sub>, where G is Gibbs free energy per mole of the gaseous species measured at the partial pressure. The condition of equilibrium is unaffected by the use of catalyst,

which increases the rate of both the forward and backward reactions to the same extent.

- c. The catalyst will increase the rate of forward reaction by  $\alpha$  and that of backward reaction by  $\beta$ .
- d. Catalyst will not alter the rate of either of the reaction.

[IIT 2006]

169. If  $\text{Ag}^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)]^+$ ;  $K_1 = 3.5 \times 10^{-3}$  and  $[\text{Ag}(\text{NH}_3)]^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+$ ;  $K_2 = 1.74 \times 10^{-3}$  the formation constant of  $[\text{Ag}(\text{NH}_3)_2]^+$  is

[IIT 2006]

- a.  $6.08 \times 10^{-6}$
- b.  $6.08 \times 10^{-6}$
- c.  $6.08 \times 10^{-9}$
- d. none of these

170. The value of  $\log_{10} K$  for a reaction  $A \rightleftharpoons B$  is (given:  $\Delta r H^\circ 298 \text{ K} = -54.07 \text{ KJ mol}^{-1}$ ,  $\Delta r S^\circ 298 \text{ K} = 10 \text{ JK}^{-1} \text{ mol}^{-1}$  and  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ;  $2.303 \times 8.314 \times 298 = 5705$ )

- a. 10
- b. 100
- c. 5
- d. 95

[IIT 2007]

## ANSWERS

### Straight Objective Type Questions

- |       |       |       |       |       |       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1. a  | 2. c  | 3. a  | 4. c  | 5. d  | 6. d  | 7. b  | 8. c  | 9. a  | 10. c | 11. a | 12. c |
| 13. b | 14. d | 15. b | 16. a | 17. c | 18. d | 19. a | 20. b | 21. a | 22. d | 23. b | 24. a |
| 25. c | 26. b | 27. a | 28. b | 29. a | 30. c | 31. d | 32. c | 33. a | 34. b | 35. c | 36. b |
| 37. d | 38. c | 39. a | 40. a | 41. d | 42. a | 43. b | 44. a | 45. d | 46. b | 47. c | 48. b |
| 49. b | 50. b | 51. d | 52. c | 53. b | 54. d | 55. a | 56. c | 57. b | 58. c | 59. b | 60. a |
| 61. c | 62. d | 63. d | 64. d | 65. a | 66. b |       |       |       |       |       |       |

### Brainteasers Objective Type Questions

- |       |       |       |       |       |       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 67. c | 68. a | 69. b | 70. b | 71. a | 72. d | 73. a | 74. b | 75. c | 76. d | 77. a | 78. a |
| 79. b | 80. b | 81. d | 82. d | 83. b | 84. c | 85. b | 86. c | 87. a | 88. c | 89. a | 90. b |
| 91. c | 92. b | 93. a | 94. b | 95. b | 96. d |       |       |       |       |       |       |

### Multiple Correct Answer Type Questions

- |                 |              |              |              |                 |              |              |
|-----------------|--------------|--------------|--------------|-----------------|--------------|--------------|
| 97. b, d        | 98. b, c, d  | 99. b, c     | 100. a, b, c | 101. b, c, d    | 102. a, b    | 103. a, c, d |
| 104. a, b, c    | 105. c, d    | 106. a, b, c | 107. c, d    | 108. a, b, c, d | 109. b, c, d | 110. b, d    |
| 111. a, b, c, d | 112. b, c, d | 113. c, d    | 114. b, c    | 115. c, d       | 116. a, b    | 117. b, d    |
| 118. a, d       | 119. b, c    | 120. a, c, d | 121. a, b, d |                 |              |              |

**Linked-Comprehension Type Questions****Comprehension 1**

122. b      123. b      124. c      125. c

**Comprehension 2**

126. b      127. a      128. b      129. c

**Comprehension 3**

130. c      131. b      132. c      133. b

**Comprehension 4**

134. b      135. c      136. a

**Assertion Reason Type Questions**

137. a      138. d      139. b      140. c

141. b      142. b      143. d      144. a

145. c      146. c      147. a      148. c

149. a      150. b      151. a      152. c

153. b      154. d

**Matrix-Match Type Questions**

155. A-(p, r,) B-(q, s), C-(t, s), D-(s, t)

156. A-(p, s) , B-(p, q, r) ,C-(p, r ), D-(p, r)

157. A-(p, s), B-(r, s), C-(r, s), D-(q)

158. A-(p), B-(r), C-(t), D-(q)

159. A-(s), B-(p), C-(q), D-(s)

160. A-(p, q), B-(q), C-(q, r, t), D-(p, r, s)

161. A-(q, s), B-(r), C-(p, s), D-(s, t)

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162. d      163. a      164. d      165. d      166. d      167. d      168. b      169. a      170. a

**Hints and Explanations****Straight Objective Type Questions**

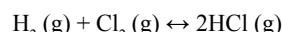
1. As the reaction is exothermic, the formation of  $\text{AB}_4$  is favoured by low temperature.

As the forward reaction is accompanied by decrease in the number of moles. So it is favoured by high pressure.

2.  $K_p = K_c$  when  $\Delta n = 0$

$$\Delta n = 2 - 2 = 0$$

So the correct option is

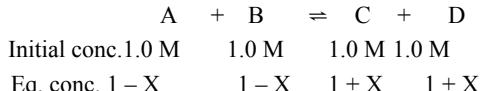


3. It is according to Le-Chatelier's principle.

As  $n_p > n_r$ .

73. This is according to Le-Chatelier's principle.

81. Let  $X$  = change in concentration of A



$$K = \frac{(1+X)(1+X)}{(1-X)(1-X)} = 100$$

$$= \frac{1+X}{1-X} = 10$$

$$= 1+X = 10 - 10X$$

$$= 11X = 9$$

$$X = 9/11 = 0.818$$

So

$$[A] = 1 - 0.818 = 0.182 \text{ M}$$

$$[C] = 1 + 0.818 = 1.818 \text{ M}$$

$$[D] = 1.818 \text{ M.}$$

83.  $K_c = \frac{[H_2]^2 [S_2]}{[H_2S]^2}$

$$[H_2] = \frac{2 \times 0.2}{2} = 0.2 \text{ mole/L}$$

$$[S_2] = 0.8/2 = 0.4 \text{ mole/L}$$

$$[H_2S] = 1 \text{ mole/L}$$

$$K_c = \frac{[0.2]^2 [0.4]}{1} = 0.016 \text{ mole/L}$$

85. Active masses of

$$NH_3 = \frac{1 \text{ g}/17 \text{ g mol}}{1 \text{ L}} = \frac{1}{17} \text{ mol/L}$$

$$N_2 = \frac{1 \text{ g}/28 \text{ g mol}}{1 \text{ L}} = \frac{1}{28} \text{ mol/L}$$

$$H_2 = \frac{1 \text{ g}/2 \text{ g mol}^{-1}}{1 \text{ L}} = \frac{1}{2} \text{ mol/L}$$

$$O_2 = 1 \text{ g}/32 \text{ g mol} = \frac{1}{32} \text{ mol/L}$$

Increasing order of active masses is:

$$1/32 < 1/28 < 1/17 < 1/2 \text{ mol/L}$$

$$O_2 < N_2 < NH_3 < H_2 \text{ that is, } 4 < 2 < 1 < 3.$$

86. When inert gas is added at constant volume, there is no effect on equilibrium. Hence none is correct.



$$1 \quad 0$$

$$1 - 0.2 \quad 0.4$$

$$= 0.8$$

Number of moles at 300 K = 1

No. of moles at 600 K = 0.8 + 0.4 = 1.2

V is constant

$$\frac{P_2}{P_1} = \frac{n_2 T_2}{n_1 T_1}$$

$$\frac{P_2}{1} = \frac{1.2 \times 600}{1 \times 300} = 2.4 \text{ atm}$$

88. As the slope of the graph is negative so  $\Delta H$  is negative as dissolution of hydrated salt is endothermic so the solute is  $CuSO_4 \cdot 5H_2O$

91.  $(1 + a) = D/d$

When  $a = 0$ ,  $D/d = 1$

When  $a$  increases,  $(1 + a)$  increases so  $D/d$  also increases

95.  $K_c = \frac{[NO_2]^2}{[N_2][O_2]^2}$

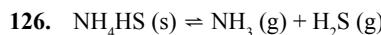
$$[N_2] = \frac{[NO_2]^2}{[O_2]^2} \frac{1}{K_c}$$

$$= \frac{(0.0152)^2}{6.0 \times 10^{-5}} = 3.85 \text{ mol/litre}$$

96.  $K_c = K_p = \frac{PCO_2}{PCO} = 6.0 \times 10^2$

If PCO is 150 torr,  $PCO_2$  can never exceed  $760 - 150 = 610$  torr. Then  $Q = 610/150 = 4.01$ . Since this is less than K, the reaction will shift in the direction of more product. Reduction will therefore occur.

### Linked-Comprehension Type Questions



$$\text{Initially } \frac{3.06}{51} \text{ mole } 0 \quad 0$$

$$= 0.06 \text{ mole } 0 \quad 0$$

$$\text{At eq. } 0.06 \times \frac{70}{100} \quad 0.06 \times \frac{30}{100} \quad 0.06 \times \frac{30}{100}$$

$$= 0.042 \quad = 0.018 \quad = 0.018$$

$$K_c = [NH_3][H_2S]$$

(As  $NH_4HS$  is solid so it is taken)

$$= \frac{0.018}{2} \times \frac{0.018}{2}$$

$$= 8.1 \times 10^{-5} \text{ mol}^2 \text{ lit}^{-2}$$

127.  $K_p = K_c (RT)^{\Delta n}$

$$= 8.1 \times 10^{-5} \times (0.082 \times 300)^2$$

$$= 0.049 \text{ atm}^2$$

128. Since  $NH_4HS(s)$  is a compound so its active mass is assumed as unity in any condition.

129. As  $\Delta n_g = 2$

that is,  $K = K_c$

131. As  $\Delta G^\circ = -2.303 RT \log_{10} KP$

$$\Delta G^\circ = -2.303 \times 2 \times 673 \times \log_{10}(1.64 \times 10^{-4})$$

On solving, we get

$$\Delta G^\circ = 11.733 \text{ kcal}$$

132. As  $Kc' = \sqrt{Kc} = \sqrt{(1.49 \times 10^{-5})}$

$$= 3.86 \times 10^{-3} \text{ lit mol}^{-1}$$

135. As  $\alpha = \frac{D-d}{(n-1)d}$

## 5.44 ■ Chemical Equilibrium

(As D = M/2 = 208.5/2 = 104.25)

$$\alpha = \frac{104.25 - 57.92}{(2 - 1) \times 57.92}.$$

On solving, we get

$$\alpha = 0.8\%$$

$$\alpha\% = 0.8 \times 100 = 80\%$$

132. As  $K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{\alpha^2}{1 - \alpha^2} \cdot P$

$$0.202 = \frac{\alpha^2}{1 - \alpha^2} \times 1.5$$

On solving, we get

$$\alpha = 0.344$$

Volume percent of  $Cl_2$  = Mole fraction  $\times 100$

$$= \frac{\alpha}{1 + \alpha} \times 100$$

$$= \frac{0.344}{1 + 0.344} \times 100 = 25.6\%$$

134.  $K_c = \frac{K_p}{(RT)^{\Delta n}}$ ;

$\Delta n = +1$ ,  $T = 700K$

$$K_c = \frac{0.76}{(0.082)(700)^{+1}}$$

$$= 0.01323 = 0.013$$

### Assertion-Reason Type Questions



Initially      2.00 atm      0 atm

Change         $-x$  atm         $+2x$  atm

At equil      (2.00-x) atm      2x atm

$$K_p = 0.76 = \frac{P_2Cl_2}{PCCl_4} = \frac{(2x)^2}{(2.00-x)}$$

$$1.52 - 0.76x = 4x^2;$$

$$4x^2 + 0.76x - 1.52 = 0$$

Using the quadratic formula ,

$$a = 4, b = 0.76, c = -1.52$$

$$x = \frac{-0.76 \pm \sqrt{(0.76)^2 - 4(4)(-1.52)}}{2(4)}$$

$$= \frac{0.76 + 4.99}{8} = 0.5287$$

$$= 0.53 \text{ atm}$$

$$\text{fraction } CCl_4 \text{ reacted} = \frac{x \text{ atm}}{2.00 \text{ atm}}$$

$$= 0.53$$

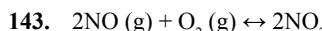
$$2.00$$

$$= 0.264 = 26\%$$

140.  $PCl_2 = 2x = 2(0.5287) = 1.06 \text{ atm}$

$$PCCl_4 = 2.00 - x = 2.00 - 0.5287$$

$$= 1.47 \text{ atm}$$



When pressure is increased then equilibrium shift in those direction where volume that is, number of moles decreases.

144. The rate of a reaction is first order of equilibrium.

150. The temperature dependence of the equilibrium constant is related to  $\Delta S^\circ$  as well as  $\Delta H^\circ$  for the reaction.

154. At equilibrium its free energy change,  $\Delta G$  which is zero for a spontaneous process,  $\Delta G < 0$

### The IIT-JEE Corner

162. Catalyst has no effect on equilibrium. Decreasing the volume or pressure has no effect because  $nr = np$ . Therefore, the equilibrium shifts in the forward direction by increasing the conc. of reactants  $CO_2(g)$ .

163. Temperature and pressure both effect equilibrium but catalyst has no effect (Le – Chatelier's principle).

164. Concentration of products increase with time so Q increases.

$$Q = \frac{[C][D]}{[A][B]}$$

165.  $\Delta n_g = 2 - 4 = -2$

$$K_p = K_c \cdot (RT)^{\Delta n}$$

$$K_c = K_p / (RT)^{\Delta n}$$

$$= \frac{1.44 \times 10^{-5}}{(0.0821 \times 773)^{-2}}$$

166.  $K_p$  (equilibrium constant) is independent of pressure and concentration

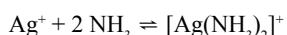
167. When volume is decreased, pressure increases and this will favour backward reaction. Thus, degree of dissociation decreases but  $K_p$  does not change since temperature is constant.

168.  $K_i = 3.5 \times 10^{-3} = \frac{[Ag(NH_3)_2]^+}{[Ag^+] [NH_3]}$

$$K_2 = 1.74 \times 10^{-3} = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}(\text{NH}_3)]^+ [\text{NH}_3]}$$

$$K_3 = K_1 \times K_2 = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+] [\text{NH}_3]^2}$$

formation constant  $K_3$  for



$$K_3 = 3.5 \times 10^{-3} \times 1.74 \times 10^{-3} \\ = 6.08 \times 10^{-6}$$

$$\Delta G^\circ = -2.303 R \log_{10} K$$

$$\Delta H^\circ = T \Delta S^\circ = -2.303 RT \log_{10} K$$

$$[-54.07 \times 10^3 - 298 \times 10]$$

$$= -2.303 \times 8.314 \times 298 \log_{10} K$$

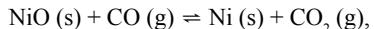
$$\log_{10} K = \frac{57050}{5705} = 10$$

## Numericals For Practice

1. Three moles of  $\text{PCl}_5$ , three moles of  $\text{PCl}_3$  and two moles of  $\text{Cl}_2$  are taken in a closed vessel. If at equilibrium the vessel has 1.5 moles of  $\text{PCl}_5$ , the number of moles of  $\text{PCl}_3$ , present in it is

- a. 8                          b. 4.5  
c. 2.1                          d. 10

2. An acid reacts with glycerine to form complex and equilibrium is established.



If the heat of reaction at constant volume for above reaction is 1200 cal more than at constant pressure and the temperature is 300 K, then which of the following expression is true?

- a.  $K_p = K_c$                           b.  $K_p < K_c$   
c.  $K_c < K_p$                                   d. None of these

3. Equivalent amounts of  $\text{H}_2$  and  $\text{I}_2$  are heated in a closed vessel till equilibrium is obtained. If 80% of the hydrogen is converted to HI, the  $K_c$  at this temperature is

- a. 14                                  b. 19  
c. 64                                          d. 0.32

4.  $\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$ . This reaction is set up in aqueous medium. We start with one mole of  $\text{I}_2$  and 0.5 mole of  $\text{I}^-$  in 1 litre flask. After equilibrium is reached, addition of excess of  $\text{AgNO}_3$  gave 0.25 mole of yellow precipitate immediately. Equilibrium constant of the reaction is

- a. 13.6                                  b. 1.33  
c. 2.26                                          d. 3.54

5. For the Equilibrium



$K_c = 8.5 \times 10^{-3}$  at  $150^\circ \text{C}$ . If 0.025 mol of IBr is placed in a 2.0 L container, what is the concentration of this substance after equilibrium is reached?

- a. 1.10M                                  b. 0.011M  
c. 0.022M                                          d. 2.20M

6. 1.6 mol of  $\text{PCl}_{5(g)}$  is placed in 4 dm<sup>3</sup> closed vessel. When the temperature is raised to 500 K, it decomposed and at equilibrium 1.2 mol of  $\text{PCl}_{5(g)}$  remains. What is the  $K_c$  value for the decomposition of  $\text{PCl}_{5(g)}$  to  $\text{PCl}_{3(g)}$  and  $\text{Cl}_{2(g)}$  at 500 K?

- a. 0.012                                          b. 0.098  
c. 0.033                                                  d. 0.056  
e. 0.002

7. Two moles of an equimolar mixture of two alcohols,  $\text{R}_1 - \text{OH}$  and  $\text{R}_2 - \text{OH}$  are esterified with one mole of acetic acid. If 80% of the acid is consumed and the quantities of ester formed under equilibrium are in the ratio of 3:2, the value of the equilibrium constant for the esterification of  $\text{R}_1 - \text{OH}$  with acetic acid is

- a. ~3.7                                          b. ~3.1  
c. ~1.3                                                  d. ~3.5

8. The value of  $K_c$  is 4.00 at  $25^\circ \text{C}$  for the following equilibrium

$\text{CH}_3\text{CO}_2\text{H} + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}_3\text{CO}_2\text{C}_2\text{O}_5 + \text{H}_2\text{O}$ . What is the concentration of  $\text{CH}_3\text{CO}_2\text{C}_2\text{O}_5$  at equilibrium if the reactants are initially 0.200 M each?

- a. 0.085 M                                          b. 0.133M  
c. 0.206M                                                  d. 0.046M

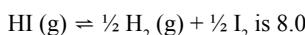
9. A mixture of  $\text{N}_2\text{O}_4 (\text{g})$  and  $\text{NO}_2 (\text{g})$  under equilibrium has an average molar mass of 76. The mole fraction

## 5.46 ■ Chemical Equilibrium

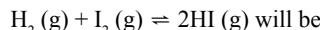
of  $\text{N}_2\text{O}_4$  at equilibrium and the percent  $\text{N}_2\text{O}_4$  dissociated are

- a. 0.7 and 50.0
- b. 0.6 and 25.0
- c. 0.8 and 45.0
- d. 0.6 and 35.0

10. The value of equilibrium constant of the reaction



The equilibrium constant of the reaction



- a. 16
- b. 1/8
- c. 1/16
- d. 1/64

11. Ammonium carbonate (solid),  $\text{H}_2\text{N.COONH}_4$  (s), dissociates to give  $\text{NH}_3(\text{g})$  and  $\text{CO}_2(\text{g})$ . The equilibrium constant for the dissociative equilibrium is  $2.8 \times 10^5 \text{ torr}^3$  at a certain temperature. The total dissociation pressure of the solid is

- a. 123.6 torr
- b. 41.2 torr
- c. 132.6 torr
- d.  $2.8 \times 10^5$  torr

12. What is  $K_c$  for the reaction  $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2(\text{g})$  if 22.3 % of the HI decomposes at 731 K?

- a.  $9.66 \times 10^{-3}$
- b.  $8.24 \times 10^{-3}$
- c.  $2.06 \times 10^{-2}$
- d.  $436 \times 10^{-3}$

13. The dissociation equilibrium of a gas  $\text{AB}_2$  can be represented as:



The degree of dissociation is 'X' and is small compared to 1. The expression relating the degree of dissociation (X) with equilibrium constant  $K_p$  and total pressure P is:

- a.  $(2K_p/P)^{1/2}$
- b.  $(K_p/P)$
- c.  $(2K_p/P)^{1/3}$
- d.  $(2K_p/P)^{1/4}$

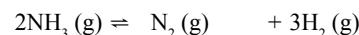
14. For the gaseous equilibrium,

$\text{A}_2(\text{g}) + \text{B}_2(\text{g}) \rightleftharpoons 2\text{AB}(\text{g})$ , the equilibrium constant at a certain temperature is 49. If an equimolar mixture of A and B is heated in a closed container to this temperature, the mole fraction of  $\text{B}_2$  in the equilibrium mixture is

- a. 1/8
- b. 3/8
- c. 1/9
- d. 2/9

15. When pure  $\text{NH}_3$  is maintained at  $480^\circ\text{C}$  and pressure of 1 atm, it dissociates to give a gaseous mixture containing 20 %  $\text{NH}_3$  by volume. The degree of dissociation of  $\text{NH}_3$  is

- a. 5/2
- b. 2/5
- c. 2/3
- d. 3/2



Initially A 0 0

At eq. A(1- $\alpha$ )  $A\alpha/2$   $3A\alpha/2$

% of  $\text{NH}_3$  by volume

$$= \frac{A(1-\alpha)}{A(1-\alpha) + \frac{A\alpha}{2} + \frac{3A\alpha}{2}} \times 100$$

According to condition,

$$\frac{1-\alpha}{1+\alpha} \times 100 = 20$$

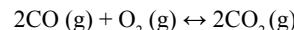
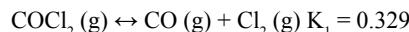
On solving, we get

$$\alpha = 2/3.$$

16. The equilibrium constants  $K_{p1}$  and  $K_{p2}$  for the reactions  $X \rightleftharpoons{} 2Y$  and  $Z \rightleftharpoons{} P+Q$ , respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressure at these equilibria is

- a. 1 : 36
- b. 1 : 1
- c. 1 : 3
- d. 1 : 9

17. At 1000 K, the equilibrium constants for the following equilibria are  $K_1$  and  $K_2$ .



$$K_2 = 2.24 \times 10^{22}$$

For the equilibrium,

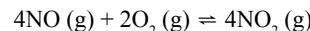
$2\text{COCl}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}_2(\text{g}) + 2\text{Cl}_2(\text{g})$ , the equilibrium constant  $K_3$  is

- a.  $2.424 \times 10^{20}$
- b.  $4.86 \times 10^{20}$
- c.  $2.424 \times 10^{21}$
- d.  $2.244 \times 10^{22}$

18. The equilibrium constant for the reaction



is  $2 \times 10^{-6}$  at  $185^\circ\text{C}$ . Then the equilibrium constant for the reaction,



at the same temperature would be

- a.  $2.5 \times 10^{11}$
- b.  $2.5 \times 10^{-5}$
- c.  $0.5 \times 10^{11}$
- d.  $2.0 \times 10^{-6}$

19. The equilibrium constant for mutarotation,  $\alpha\text{-D-glucose} \rightleftharpoons \beta\text{-D-glucose}$  is 1.8. The percentage of the  $\alpha$ -form in the equilibrium mixture is

- a. 64.5
- b. 35.7
- c. 53.7
- d. 44.8

20. What is  $K_c$  for the reaction  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$  if at  $9^\circ\text{C}$  a one liter solution of chloroform contains 0.250 mol of  $\text{N}_2\text{O}_4$  and  $1.64 \times 10^{-3}$  mol of  $\text{NO}_2$ ?

- a.  $634 \times 10^5$       b.  $6.54 \times 10^{-4}$   
 c.  $1.07 \times 10^{-5}$       d.  $2.26 \times 10^{-6}$
21. The concentration of  $\text{H}_3\text{O}^+$  ions in a mixture of 0.05 M acetic acid and 0.5 M sodium acetate is ( $K_a$  for acetic acid is  $1.5 \times 10^{-5}$ )  
 a.  $1.1 \times 10^{-6}$       b.  $1.5 \times 10^{-4}$   
 c.  $1.5 \times 10^{-6}$       d.  $2.0 \times 10^{-4}$
22. The equilibrium constant for the reaction  
 $\text{SO}_3(\text{g}) \leftrightarrow \text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$   
 is  $K_c = 4.9 \times 10^{-2}$ . the value of  $K_c$  for the reaction  
 $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2\text{SO}_3(\text{g})$   
 will be  
 a. 416      b.  $2.40 \times 10^{-3}$   
 c.  $9.8 \times 10^{-2}$       d.  $4.9 \times 10^{-2}$
23. The vapour density of  $\text{N}_2\text{O}_4$  at a certain temperature is 30. The percentage dissociation of  $\text{N}_2\text{O}_4$  at this temperature is  
 a. 25      b. 50  
 c. 75      d. 100
24. Ammonium carbamate when heated to  $200^\circ\text{C}$  gives a mixture of  $\text{NH}_3$  and  $\text{CO}_2$  vapours with a density of 16.0. What is the degree of dissociation of ammonium carbamate?  
 a. 1/2      b. 3/2  
 c. 1      d. 2  
 e. 5/2
25. At a certain temperature, the vapour density of  $\text{PCl}_5$  in equilibrium with  $\text{PCl}_3$  and  $\text{Cl}_2$  is 90. The degree of dissociation of  $\text{PCl}_5$  (mol. wt. 208.5) is  
 a. 15.8      b. 81.5  
 c. 8.5      d. 31.5
26. (A) At  $27^\circ\text{C}$ ,  $\text{NO}$  and  $\text{Cl}_2$  gases are introduced in a 10 litre flask such that their initial partial pressures are 20 and 16 atm respectively. The flask already contains 24 g of magnesium. After some time, the amount of magnesium left was 0.2 moles due to the establishment of following two equilibria  
 $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g})$   
 $\text{l}_2(\text{g}) + \text{Mg}(\text{s}) \rightleftharpoons \text{MgCl}_2(\text{s})$ ,  $K_p = 0.2 \text{ atm}^{-1}$   
 The final pressure of  $\text{NOCl}$  would be  
 a. 18.06 atm      b. 81.06 atm  
 c. 28.18 atm      d. 45.86 atm
27. Solid  $\text{NH}_4\text{HS}$  is introduced into an evacuated flask at  $24^\circ\text{C}$ . The following reaction concentration of  $\text{PH}_3$ ?



At equilibrium the total pressure (for  $\text{NH}_3$  and  $\text{H}_2\text{S}$  taken together) was 0.614 atm. What is  $K_p$  for this equilibrium at  $24^\circ\text{C}$ ?

- a. 9.43      b. 94.30  
 c. 0.0943      d. 0.943

28. If, for an equilibrium, the equilibrium constants at  $27^\circ\text{C}$  and  $127^\circ\text{C}$  are respectively  $K_1$  and  $K_2$  and if  $\Delta H^\circ$  for the forward reaction in the above temperature range is 4576 cal,  $\log_{10} K_2/K_1$  is

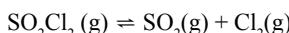
- a. 5/6      b.  $-5/6$   
 c.  $\frac{4576}{300 \times 400}$       d.  $\frac{4576}{300 \times 400}$ .

29. The  $\text{CaCO}_3$  is heated in a closed vessel of volume 1 litre at  $600 \text{ K}$  to form  $\text{CaO}$  and  $\text{CO}_2$ . The minimum weight of  $\text{CaCO}_3$  required to establish the equilibrium



- a. 2.45      b. 10.57 g  
 c. 4.57 g      d. 14.75 g

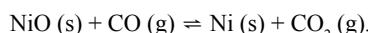
30. When 2.00 mol of  $\text{SO}_2\text{Cl}_2$  is placed in a 2.00-L flask at  $303 \text{ K}$ , 56 percent of the  $\text{SO}_2\text{Cl}_2$  decomposes to  $\text{SO}_2$  and  $\text{Cl}_2$ :



calculate  $K_c$  for this reaction at this temperature.

- a. 0.71      b. 0.355  
 c. 3.55      d. 0.623

31. For the reaction,



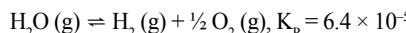
$\Delta G^\circ_p (\text{J mol}^{-1}) = -20700 - 12T$ . Nickel is exposed to a current of hot carbon dioxide. The product gases at equilibrium at 1 atm pressure contain 500 ppm of carbon monoxide, the temperature should be

- a. 273 K      b. 204 K  
 c. 474 K      d. 404 K

32. mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  has a vapour density of 38.3 at  $300 \text{ K}$ . What is the number of moles of  $\text{NO}_2$  in 100 g of the mixture?

- a. 0.043      b. 3.43  
 c. 4.34      d. 0.436  
 e. 1.43

33. Steam at pressure of 2 atm is passed through a furnace at  $2000 \text{ K}$  where in the reaction



occurs. The percentage of oxygen in the exit stream would be

## 5.48 ■ Chemical Equilibrium

- |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>a. 0.08                    b. 0.16<br/> c. 0.36                    d. 0.004</p> <p><b>34.</b> A 6.00-L vessel contained 0.0222 mole of <math>\text{PCl}_3</math>, 0.0189 mole of <math>\text{PCl}_5</math>, and 0.01044 mole of <math>\text{Cl}_2</math> at <math>230^\circ\text{C}</math> in an equilibrium mixture. Calculate the value of <math>K_{\text{eq}}</math> for the reaction</p> $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$ <p>a. 24.45                    b. 48.9<br/> c. 4.89                    d. 52.6</p> | <p><b>35.</b> What per cent of <math>\text{CO}_2</math> in air is just sufficient to prevent loss in weight when <math>\text{CaCO}_3</math> is heated at <math>100^\circ\text{C}</math>? Equilibrium constant <math>K_p</math> for</p> $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ <p>is 0.0095 atm at <math>100^\circ\text{C}</math>.</p> <p>a. 1.85%                    b. 0.15 %<br/> c. 0.05%                    d. 0.95 %</p> |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

### ANSWER KEYS

Q.	Ans.								
1.	b	2.	b	3.	c	4.	b	5.	b
6.	c	7.	a	8.	b	9.	b	10.	d
11.	a	12.	c	13.	d	14.	c	15.	c
16.	a	17.	c	18.	a	19.	b	20.	c
21.	c	22.	a	23.	b	24.	c	25.	a
26.	a	27.	c	28.	a	29.	c	30.	a
31.	d	32.	d	33.	a	34.	b	35.	a

## Hints and Explanations

**1.**  $\text{PCl}_{5(\text{g})} \rightleftharpoons \text{PCl}_{3(\text{g})} + \text{Cl}_{2(\text{g})}$   
3      2      1 (Initially)  
 $(3-x)$   $(3+x)$   $(2+x)$  (At equilibrium)  
Given that,  $(3-x) = 1.5$   
Therefore no of moles of  $\text{PCl}_{3(\text{g})}$  present is  
 $= 3 + 1.5 = 4.5$

**2.** As  $\Delta E - \Delta H = 1200$  cal

$$\Delta H = \Delta E + \Delta n RT$$

$$\Delta n RT = \Delta H - \Delta E = -1200$$

$$\text{So } \Delta n = -2$$

$$K_p = K_c (RT)^{\Delta n}$$

$$\frac{K_p}{K_c} = 1.648 \times 10^{-3}$$

Therefore,  $K_p < K_c$

**3.**  $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$   
Initial a      a mol  
At eq. a - 0.8a      a - 0.8a       $2 \times 0.8a$   
 $= 0.2a$        $= 0.2a$        $= 1.6a$   
molar-  $\frac{0.2a}{V}$        $\frac{0.2a}{V}$        $\frac{1.6a}{V}$   
conc.

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.6a/V)^2}{(0.2a/V)(0.2a/V)}$$

$$= \frac{(1.6)^2}{(0.2)^2} = \frac{2.56}{0.04} = 64$$

**4.**  $\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$   
Initial conc. 1      0.5      0  
Eq. conc.  $(1-X)$   $(0.5-X)$       X  
 $0.5 - X = 0.25$   
 $X = 0.25$

$$K_{\text{eq}} = \frac{[\text{I}_3^-]}{[\text{I}_2] [\text{I}^-]} = \frac{0.25}{0.25 \times 0.75} = 1.33$$

6. 1.6 mol of  $\text{PCl}_3$  is placed in 4 dm<sup>3</sup> closed vessel



1.6 mol 0 0 (Initially)

$(1.6 - x) \times \text{mol} \times \text{mol}$  (At equilibrium)

Given that  $1.6 - x = 1.2$

As  $x = 0.4$  mol

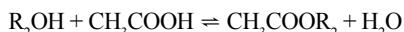
$$\text{Therefore, } [\text{PCl}_{3}] = \frac{1.2}{4} = 0.3, [\text{PCl}_3] = \frac{0.4}{4} = 0.1$$

$$\text{and } [\text{Cl}_2] = \frac{0.4}{4} = 0.1$$

$$\text{So, } K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{0.1 \times 0.1}{0.3} = 0.033$$

7.  $\text{R}_1\text{OH} + \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COOR}_1 + \text{H}_2\text{O}$

$(1 - X)(1 - X - Y) X (X + Y)$



$(1 - Y)(1 - X - Y) Y (X + Y)$

As in esterification process the amount of acid consumed = 80%

So  $X + Y = 0.8$

$X/Y = 3/2$

$X = 0.48$  and  $Y = 0.32$

For first esterification process,

$$\text{Equilibrium constant} = \frac{X(X+Y)}{(1-X)(1-X-Y)}$$

$$K_{c1} = \frac{0.48 \times 0.8}{0.52 \times 0.2}$$

$$K_{c1} \approx 3.7$$

9. Molar masses:  $\text{N}_2\text{O}_4 = 96$

$$\text{NO}_2 = 46$$

$$M = x \cdot 96 + (1 - x) 46 = 76$$

$$96x + 46 - 46x = 76$$

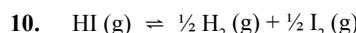
$$x = 0.6 = [\text{N}_2\text{O}_4] \text{ eq.}$$



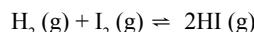
Equilibrium mixture contains 0.6 moles of  $\text{N}_2\text{O}_4$  and 0.4 moles  $\text{NO}_2$ .

$$\text{Initial moles of } \text{N}_2\text{O}_4 = 0.6 + \frac{0.4}{2} = 0.8 \text{ moles}$$

$$\text{Percentage of dissociation} = \frac{0.2 \times 100}{0.8} = 25$$

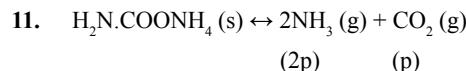


$$K = \frac{[\text{H}_2]^{\frac{1}{2}}}{[\text{I}_2]^{\frac{1}{2}} [\text{HI}]} = 8$$



$$K' = \frac{[\text{HI}]^2}{[\text{H}_2] [\text{I}_2]} = (1/8)^2$$

$$K' = 1/64.$$



(2p) (p)

$$K_p = p_{\text{NH}_3}^2 p_{\text{CO}_2} = (2p)^2 p = 4p^3$$

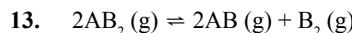
$$= 2.8 \times 10^5 \text{ torr}^3.$$

$$p^3 = 0.7 \times 10^5 \text{ torr}^3 = 70 \times 10^3 \text{ torr}^3$$

$$p = 41.2 \text{ torr}$$

Total dissociation pressure = 3p

$$= 123.6 \text{ torr}$$



2 0 0 initially

$2(1 - X) 2X X$  at. eq.

Amount of moles at equilibrium

$$= 2(1 - X) + 2X + X = 2 + X$$

$$K_p = \frac{[\text{P}_{\text{AB}}]^2 [\text{P}_{\text{B}_2}]}{[\text{P}_{\text{AB}_2}]^2}$$

$$K_p = \frac{\frac{2X}{2+X} \times P^2 \times \frac{X}{2+X} \times P}{\frac{2(1-X)}{2+X} \times P^2}$$

$$K_p = \frac{\frac{4X^3}{2+X} \times P}{4(1-X)^2}$$

$$K_p = \frac{4X^3 \times P}{2} \times \frac{1}{4}$$

(As  $1 - X \approx 1$  &  $2 + X \approx 2$ )

$$X = (8K_p/4P)^{1/3} = (2K_p/P)^{1/3}$$



$(a - x) (a - x) (2x)$

(total number of moles = 2a)

$$\text{Equilibrium constant (K}_p \text{ or K}_c) = \frac{4x^2}{(a - x)^2} = 49$$

Total number of moles at equilibrium = 2a

## 5.50 ■ Chemical Equilibrium

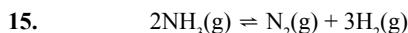
$$\frac{2x}{a-x} = 7; \frac{a-x}{2x} = \frac{1}{7}$$

$$\frac{a}{2x} - \frac{1}{2} = \frac{1}{7}; \frac{a}{2x} = \frac{9}{14}.$$

$$2x/a = 14/9$$

$$x/a = 7/9$$

$$a - x/2a = 1/9.$$



Initially	A	O	O
At eq.	$A(1-\alpha)$	$A\alpha/z$	$3A\alpha/2$

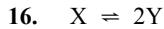
% of  $\text{NH}_3$  by volume

$$= \frac{A(1-\alpha)}{A(1-\alpha) + \frac{A\alpha}{2} + \frac{3A\alpha}{2}}$$

According to conditions

$$\frac{1-\alpha}{1-\alpha} \times 100 = 20; \text{ on solving we get}$$

$$\alpha = 2/3$$



1	0
$(1-x)$	$2x$

$$K_{p_1} = \frac{(2x)^2}{(1-x)} (P_1/1+x)^1$$

$$Z = P + Q$$

1	0	0
$(1-x)$	$x$	$x$

$$K_{p_2} = \frac{(x)^2}{(1-x)} (P_2/1+x)^1$$

$$\frac{4 \times P_1}{P_2} = \frac{1}{9}$$

On solving, we get

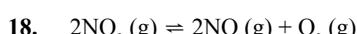
$$P_1 : P_2 = 1 : 36$$

17. The first equilibrium is multiplied by 2 and added to equilibrium (2) to get equilibrium (3).

$$K_3 = (K_1)^2 \times K_2$$

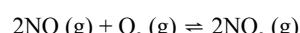
$$K_3 = (0.329)^2 \times 2.24 \times 10^{22}$$

$$= 0.2424 \times 10^{22} = 2.424 \times 10^{21}$$



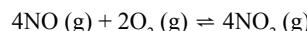
$$K = 2 \times 10^{-6}$$

For the reverse reaction,



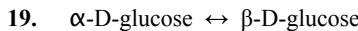
$$K = \frac{1}{2 \times 10^{-6}}.$$

Multiplying with 2,



$$K = (1/2 \times 10^{-6})^2$$

$$= 0.25 \times 10^{12} = 2.5 \times 10^{11}$$



$$(1-x) \text{ mole} \quad x \text{ mole}$$

$$K = \frac{x}{1-x} = 1.8$$

$$x = 1.8 - 1.8x$$

$$2.8x = 1.8$$

$$x = 1.8/2.8 = 9/14 = 0.643$$

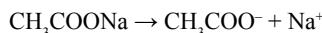
$$(1-x) = 0.357$$

$\alpha$ -form in the equilibrium mixture = 35.7%



$$\text{Initially } 0.05 \text{ M} \quad 0 \quad 0$$

$$\text{At eq. } (0.05-X) \quad X \quad X$$



$$\text{Initially } 0.05 \text{ M} \quad 0 \quad 0$$

$$\text{At eq. } 0 \quad 0.5 \quad 0.5$$

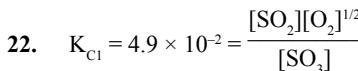
$$[\text{CH}_3\text{COO}^-] = 0.5 + X = 0.5$$

$$[\text{CH}_3\text{COOH}] = 0.05 - X = 0.05$$

$$1.5 \times 10^{-5} = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

$$= \frac{0.5 \times [\text{H}_3\text{O}^+]}{0.05}$$

$$[\text{H}_3\text{O}^+] = \frac{1.5 \times 10^{-5} \times 0.05}{0.5} = 1.5 \times 10^{-6} \text{ M}$$



$$K_{\text{C2}} = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}.$$

$$K_{\text{C2}} = (1/K_{\text{Cl}})^2 = (1/4.9 \times 10^{-2})^2 = 416.5$$



$$\text{Vapour density} = \frac{92}{2} = 46$$

$$\text{Density} = 30$$

$$\alpha = \frac{D-d}{d} = \frac{46-30}{30} = 0.5$$

So degree of dissociation = 50%.



Initial 1 mole

After diss.  $1 - \alpha \quad 2\alpha \quad \alpha$

Total =  $2 + 1\alpha$

Theoretical density (d)  $\propto \frac{1}{V}$ .

Observed density (d)  $\propto \frac{1}{(1 + 2\alpha)V}$ .

$D/d = 1 + 2\alpha$

$$\alpha = \frac{1}{2} \frac{(D - d)}{d}$$

$$= \frac{1}{2} \frac{(48 - 16.0)}{16.0} = 1.0$$

25. Degree of dissociation

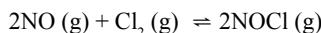
$$\alpha = \frac{(V.D)_t - (V.D)_0}{(n - 1)(V.D)_0}$$

$$(V.D)_t = \frac{208.5}{2} = 104.25$$

$$\alpha = \frac{104.25 - 90}{90} = 0.158$$

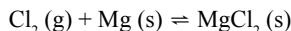
$$26. K_p = 0.2 = \frac{1}{\text{PCl}_2}.$$

( $\text{PCl}_2$  at equilibrium = 5 atm)



Initially 20 16 0

At eq. 20-2X 16-X-Y 2X



Initially 16 1 0

At eq. 16-X-Y 1-Y Y'

$$= 0.2$$

$$Y' = 0.8$$

(As Y' is in moles while Y is pressure in atm)

$$Y = \frac{0.8 \times 0.082 \times 300}{10} = 1.98$$

$$\text{As } 16 - X - Y = 5$$

On solving, we get

$$X = 9.03$$

$$\text{So } P_{\text{NOCl}} = 18.06$$

$$27. K_p = P_{\text{NH}_3} \times P_{\text{H}_2\text{S}}; P_t = 0.614 \text{ atm}$$

If the equilibrium amounts of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  are due solely to the decomposition of  $\text{NH}_4\text{HS(s)}$ , the equilibrium pressure of the two gases are equal, and each is  $\frac{1}{2}$  of the total pressure.

$$P_{\text{NH}_3} = P_{\text{H}_2\text{S}} = 0.614 \text{ atm}/2 = 0.307 \text{ atm}$$

$$K_p = (0.307)^2 = 0.0943$$

$$28. \log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303 \text{ R}} \left[ \frac{1}{300} - \frac{1}{400} \right]$$

$$2.303 \text{ R} = 2.303 \times 1.987$$

$$= 4.576 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$\Delta H^\circ = 4576 \text{ cal mol}^{-1}$$

$$\log K_2/K_1 = 1000 (1/1200) = 10/12$$

$$= 5/6.$$

$$29. \text{ As } K_p = P_{\text{CO}_2} = 2.25 \text{ atm}$$

So number of moles of  $\text{CO}_2$

$$= \frac{2.25 \times 1}{0.0821 \times 600}.$$

The minimum moles of  $\text{CaCO}_3$  needed

$$= 0.0457$$

The minimum weight of  $\text{CaCO}_3$  needed

$$= 0.0457 \times 100 = 4.57 \text{ g}$$

30.  $[\text{SO}_2\text{Cl}_2] = 2.00 \text{ mol}/2.00 \text{ L} = 1.00 \text{ M}$ . The change in  $[\text{SO}_2\text{Cl}_2]$ ,  $x = 0.56$  (1.00 M) = 0.56 M



Initially 1.00M 0 0

Change -0.56M +0.56M + 0.56 M

At quil. 0.44 M +0.56 M + 0.56 M

$$K_c = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]}$$

$$= \frac{(0.56)^2}{0.44}$$

$$= 0.7127 = 0.71 \text{ M}$$

$$31. \text{ As } \text{PCO} \ll \text{PCO}_2$$

$$\text{So } K_p = \frac{\text{PCO}_2}{\text{PCO}} = \frac{1}{500 \times 10^{-6}} = 2000$$

$$\text{As } 2.303 \text{ RT} \log_{10} K_p = -\Delta G_p^\circ$$

$$2.303 \times 8.314 \times T \times \log_{10} 2000 = 20700 + 12T$$

On solving, we get

$$T = 404.3 \text{ K}$$

$$32. \text{ Assume } \text{NO}_2 = X \text{ g}$$

$$\text{Then } \text{N}_2\text{O}_4 = (100 - X) \text{ g}$$

$$\text{Moles of } \text{NO}_2 = X/46$$

## 5.52 ■ Chemical Equilibrium

$$\text{Moles of N}_2\text{O}_4 = \frac{100 - X}{92}$$

Mole fraction of NO<sub>2</sub>

$$= \frac{X/46}{X/46 + (100 - X)/96}.$$

$$= \frac{X}{46} \times \frac{92}{100 + X} = \frac{2X}{100 + X}.$$

Molar mass of mixture

$$= \frac{2X}{100 + X} \times 46 + \frac{100 - X}{100 + X} \times 92$$

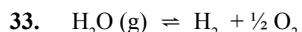
$$= \frac{9200}{100 + X}.$$

$$\frac{9200}{100 + X} = 2 \times 38.3 = 76.6$$

$$76.6X = 9200 - 7660 = 1540$$

$$X = 20.10 \text{ g}$$

$$\text{So moles of NO}_2 = \frac{20.10}{46} = 0.436$$



Initially 2 atm 0 0

At eq. 2 - X X X/2

$$\frac{X(X/2)^{1/2}}{2 - X} = 6.4 \times 10^{-5}$$

$$\frac{X^{3/2}}{\sqrt{2}(2 - X)} = 6.4 \times 10^{-5}$$

As dissociation of H<sub>2</sub>O is very less so

$$P_{H_2O} \approx 2 \text{ atm}$$

that is, 2 - X ≈ 2

$$X^{3/2} = 2\sqrt{2} \times 6.4 \times 10^{-5}$$

$$X^{3/2} = (2 \times 10)^{3/2} \times 10^{-6}$$

On solving, we get

$$X = 2 \times 16 \times 10^{-4} = 0.0032$$

So % of O<sub>2</sub> in the exit stream

$$= \frac{0.0032}{2} \times 100 = 0.08 \%$$

35. For CaCO<sub>3</sub>(s) ⇌ CaO(s) + CO<sub>2</sub>(g)

$$K_p = P_{CO_2} = 0.0095 \text{ atm}$$

As atmospheric pressure = 1 atm

$$\text{So \% of CO}_2 \text{ in air} = \frac{P_{CO_2}}{P_{\text{Total}}} \times 100 = 0.95\%$$

Therefore, to prevent the decomposition of CaCO<sub>3</sub> at 100°C of CO<sub>2</sub> in air must be greater than 0.95%.

# CHAPTER 5B

# Ionic Equilibrium

## Chapter Contents

Solubility product, common ion effect, pH and buffer solutions; Acids and bases (Bronsted and Lewis concepts); Hydrolysis of salts, and Various levels of multiple-choice questions.

## IONIC EQUILIBRIUM

### Type of Substances

Substances are of two types:

1. Non-Electrolyte: Their aqueous solution or molten state does not conduct electricity.  
Example, solution of urea, glucose, sugar, glycerine etc.
2. Electrolyte: Their aqueous or molten state conducts electricity.

**Strong Electrolyte:** These are much ionized in water, and hence show more conduction. Example, Strong acids like HCl,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , strong bases like MOH,  $\text{M}(\text{OH})_2$  Example, KOH, NaOH etc., and salt of strong acid or strong base like NaCl,  $\text{CH}_3\text{COONa}$ ,  $\text{NH}_4\text{X}$  etc.

**Weak Electrolyte:** These are less ionized in water so show less conduction. Example, weak acids like  $\text{CH}_3\text{COOH}$ , HCN,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{CO}_3$ , weak

bases like  $\text{NH}_4\text{OH}$  and their salts like  $\text{NH}_2\text{CN}$ ,  $\text{CH}_3\text{COONH}_4$  etc.,

**Degree of Ionization:** It is the extent to which an electrolyte gets ionized in a solvent. It is shown by  $\alpha$  or x.

$$\alpha = \frac{\text{number of molecules dissociated}}{\text{total number of molecules}}$$

**$\alpha$  depends upon**

- Nature of solute and solvent: For strong electrolytes,  $\alpha$  is more than that for weak electrolytes.
- $\alpha \propto$  Dielectric constant of solvent  
That is, greater the dielectric constant of a solvent more will be ionization of electrolyte in it.
- The degree of dissociation of weak electrolyte  $\alpha$  Dilution that is  $\alpha$  is maximum at infinite dilution.
- $\alpha \propto 1/\text{Concentration}$
- $\alpha \propto \text{Temperature}$

## Ostwald Dilution Law

It is law of mass action for weak electrolytes and dilute solutions. It is not applicable for strong electrolytes or highly concentrated solutions.

### For a Binary Weak Electrolyte



$$\begin{array}{ccc} 1 & 0 & 0 \end{array}$$

$$\begin{array}{ccc} 1-\alpha & \alpha & \alpha \end{array}$$

$$(1-\alpha)/V \quad (\alpha/V) \quad (\alpha/V)$$

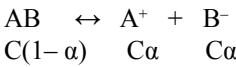
$$so \quad K = \frac{\alpha^2 / V^2}{(1-\alpha)/V} = \frac{\alpha^2}{(1-\alpha)V}$$

$$K = \frac{\alpha^2}{V} \text{ or } \alpha^2 = KV \text{ or } \alpha = \sqrt{KV}$$

$$\alpha \propto = \sqrt{V}$$

that is, at constant temperature, degree of dissociation is directly proportional to the square root of its dilution.

- If 'C' is the concentration then



$$K = \frac{C \alpha^2}{(1-\alpha)}$$

$$K = C \alpha^2 \quad \text{or} \quad \alpha^2 = K/C$$

$$\alpha = \sqrt{(K/C)}$$

$$\text{i.e., } \alpha \propto \sqrt{1/C}$$

that is, at constant temperature, degree of dissociation is inversely proportional to the square root of its concentration.

- $\alpha = \frac{\lambda v}{\lambda \infty} \text{ or } \frac{\Delta v}{\Delta \infty}$

Here  $\lambda v$  or  $\Delta v$  is equivalent conductivity at  $V$  dilution, and  $\lambda \infty$  or  $\Delta \infty$  is equivalent conductivity at infinite dilution.

- $\lambda v = K v \times V$

Here  $K v$  = specific conductivity

$V$  = dilution

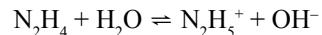
- $\lambda \infty = \lambda c + \lambda a$

Here  $\lambda c$  and  $\lambda a$  are the ionic mobilities of cation and anion respectively.

## Illustrations

- 0.16 g of  $N_2H_4$  is dissolved in water and the total volume is made up to 500 ml. Calculate the percentage of  $N_2H_4$  that has reacted with water in this solution. The  $K_b$  for  $N_2H_4$  is  $4.0 \times 10^{-6} M$ .

### Solution



$$\begin{array}{ccc} \text{Before dissociation} & 1 & 0 \\ & 0 & 0 \end{array}$$

$$\begin{array}{ccc} \text{After dissociation} & 1-\alpha & \alpha \\ & \alpha & \alpha \end{array}$$

$$K_b = \frac{C \alpha^2}{(1-\alpha)}.$$

$$1-\alpha = 1$$

$$K_b = C\alpha^2$$

$$[N_2H_4] = C = \frac{0.16 \times 1000}{32 \times 500} = 0.01$$

$$\text{Given: } K_b = 4 \times 10^{-6} M$$

$$\alpha^2 = \frac{4 \times 10^{-6}}{0.01} = 4 \times 10^{-4}$$

$$\alpha = 2 \times 10^{-2}$$

$$\alpha = 0.02 \text{ or } 2\%$$

- An aqueous solution of aniline of concentration  $0.24 M$  is prepared. What concentration of sodium hydroxide is needed in this solution so that anilinium ion concentration remains at  $1 \times 10^{-8} M$ ?  $K_a$  for  $C_6H_5NH_3^+$  is  $2.4 \times 10^{-5} M$ .

### Solution



$$K_b = \frac{[C_6H_5NH_3^+] [OH^-]}{[C_6H_5NH_2]} \quad \dots \quad (i)$$

$$K_b \text{ for } C_6H_5NH_2 = \frac{K_w}{K_a \text{ for } C_6H_5NH_3^+}.$$

$$= \frac{10^{-14}}{2.4 \times 10^{-5}} \quad \dots \quad (ii)$$

As dissociation of  $C_6H_5NH_2$  occurs in presence of  $NaOH$  so dissociation of  $C_6H_5NH_2$  will suppress.

$$[C_6H_5NH_2] = 0.24$$

$$[C_6H_5NH_3^+] = 10^{-8}$$

$$[OH^-] = ?$$

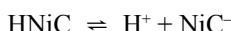
$$\text{So } \frac{10^{-14}}{2.4 \times 10^{-5}} = \frac{10^{-8} \times [\text{OH}^-]}{0.24}$$

$$[\text{OH}^-] = \frac{0.24 \times 10^{-14}}{2.4 \times 10^{-5} \times 10^{-8}} = 0.01$$

$$[\text{NaOH}] = 0.01 \text{ M}$$

3. Nicotinic acid ( $K_a = 1.4 \times 10^{-5}$ ) is represented by the formula  $\text{HNiC}$ . Calculate its per cent dissociation in a solution which contains 0.10 mole of nicotinic acid per 2.0 litre of solution.

### Solution



$$\begin{array}{ccc} 1 & 0 & 0 \\ (1-\alpha) & \alpha & \alpha \end{array}$$

$$C = \frac{0.1}{2} = 5 \times 10^{-2} \text{ mole litre}^{-1}$$

$$K_a = 1.4 \times 10^{-5}$$

$$K_a = \frac{C \alpha^2}{(1-\alpha)} = C\alpha^2$$

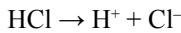
(As  $1 - \alpha \approx 1$ )

$$\alpha = \sqrt{(K_a / C)} = \frac{\sqrt{(1.4 \times 10^{-5})}}{\sqrt{(5 \times 10^{-2})}}$$

$$= 1.67 \times 10^{-2} \text{ or } 1.67 \%$$

4. A solution contains 0.1 M  $\text{H}_2\text{S}$  and 0.3 M HCl. Calculate the conc. of  $\text{S}^{2-}$  and  $\text{HS}^-$  ions in solution. Given  $K_{a_1}$  and  $K_{a_2}$  for  $\text{H}_2\text{S}$  are  $10^{-7}$  and  $1.3 \times 10^{-13}$  respectively.

### Solution



Due to common ion effect the dissociation of  $\text{H}_2\text{S}$  is suppressed and the  $[\text{H}^+]$  in solution is due to HCl.

$$K_{a_1} = \frac{[\text{H}^+] [\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$10^{-7} = \frac{[0.3] [\text{HS}^-]}{[0.1]} \quad [\text{as } [\text{H}^+] \text{ from HCl} = 0.3]$$

$$[\text{HS}^-] = \frac{10^{-7} \times 0.1}{0.3} = 3.3 \times 10^{-8} \text{ M}$$

$$K_{a_1} = \frac{[\text{H}^+] [\text{HS}^-]}{[\text{H}_2\text{S}]} \text{ and } K_{a_2} = \frac{[\text{H}^+] [\text{S}^{2-}]}{[\text{HS}^-]}$$

$$K_{a_1} \times K_{a_2} = \frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

$$10^{-7} \times 1.3 \times 10^{-13} = \frac{[0.3]^2 [\text{S}^{2-}]}{[0.1]}$$

$$[\text{S}^{2-}] = \frac{1.3 \times 10^{2-} \times 0.1}{0.09} = 1.44 \times 10^{-20} \text{ M}$$

### Common Ion Effect

The value of degree of dissociation for a weak electrolyte is decreased by the addition of a strong electrolyte having common ion.

As a result of this effect the concentration of the uncommon ion of the weak electrolyte decreases.

Example, – (1)



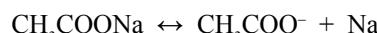
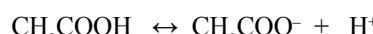
Weak



Common ion

Here  $\alpha$  for  $\text{NH}_4\text{OH}$  will be decreased by  $\text{NH}_4\text{Cl}$ .

(2)



Common ion

Here  $\alpha$  for  $\text{CH}_3\text{COOH}$  will be decreased by  $\text{CH}_3\text{COONa}$ .

■ Solubility of a partially soluble salt decreases due to common ion effect. For example, presence of  $\text{AgNO}_3$  or  $\text{KCl}$  decreases solubility of  $\text{AgCl}$  in water.

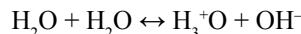
■ Salting out of soap by addition of NaCl.

■ Purification of NaCl by passing HCl gas.

**Isohydric Solution:** These are the solutions having same concentration of common ions.

### Ionic Product of Water

It is the product of the molar concentrations of  $\text{H}^+$  or  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions. It is denoted by  $K_w$ .



$$K_w = [\text{H}_3\text{O}^+] \cdot [\text{OH}^-]$$

$[\text{H}^+]$  Or

Here  $K_w$  = Ionic product of water or auto protonation constant of water

## 5.56 ■ Ionic Equilibrium

- $K_w = K_a \cdot K_b$
- $pK_w = -\log_{10} K_w$
- $K_w = K_a \times K_b$
- $pK_w = pK_a + pK_b$
- At  $25^\circ C$  :  $K_w = 1 \times 10^{-14}$

$$pK_w = 14$$

The value of  $K_w$  increases with the increase of temperature.

For example, at  $98^\circ C$ ,  $K_w$  is  $1 \times 10^{-12}$ .

### pH Scale

It was introduced by Sorrenson to measure acidity or basicity of a solution. pH Potential de –  $H^+$ -ion concentration.

It is given as

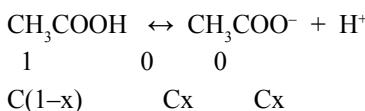
$$[H^+] = 10^{-pH}$$

$$pH = -\log_{10} [H^+]$$

pH of aqueous solution is equal to –ve log of  $H^+$  ( $H_3O^+$ ) concentration in mole/litre.

- $pH = \log_{10} \frac{1}{[H^+]}$

**pH of Weak Acid** In case of a weak acid like acetic acid



$$K = Cx^2$$

$$x = \sqrt{(K_a / C)}$$

$$[H^+] = Cx = C\sqrt{(K_a/C)} \approx \sqrt{K_a C}$$

$$pH = -\log_{10} Cx$$

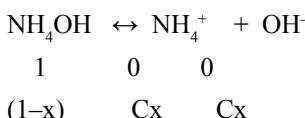
$$pH = -\log_{10} \sqrt{K_a C}$$

Here C = Molar concentration of acid

x = Degree of dissociation

$K_a$  = Dissociation constant of an acid

### pH of Weak Base



$$[\text{OH}^-] = Cx = \sqrt{K_b C}$$

$$pOH = -\log_{10} Cx$$

$$pOH = -\log_{10} \sqrt{K_b C}$$

Here  $K_b$  = dissociation constant of a base.

### REMEMBER

- pH of strong acid or base does not depend upon temperature
- pH of weak acid decreases with increase in temperature due to increase in ionization.
- pH of weak base increases with increase in temperature due to increase in ionisation or  $[\text{OH}^-]$  ion concentration.

### pOH

$$[\text{OH}^-] = 10^{-pOH}$$

$$pOH = -\log_{10} [\text{OH}^-] \text{ or } \frac{1}{\log_{10} [\text{OH}^-]}.$$

- $pH + pOH = 14$
- $pH + pOH = pK_w$
- $pK_a = -\log_{10} K_a$
- $pK_a \propto \frac{1}{K_a} \propto \frac{1}{\text{Acidic Strength}}$ .
- $pK_b = -\log_{10} K_b$
- $pK_b \propto \frac{1}{K_b} \propto \frac{1}{\text{Basic strength}}$ .
- pK: –ve log of dissociation constant.
- A weak acid has high  $pK_a$
- A weak base has high  $pK_b$ .

### To Find the Nature of Solution

- If  $[H^+] > 10^{-7}$ , pH is less than 7 and the solution is acidic.
- If  $[H^+] = 10^{-7}$ , pH is 7 and the solution is neutral.
- If  $[H^+] < 10^{-7}$ , pH is more than 7 and the solution is basic.

## pH Range of Some Substances

Substance	pH – range
Gastric	1 – 3.0
Soft drink	2 – 4.0
Lemons	2.2 – 2.4
Vinegar	2.4 – 2.4
Urine	4.8 – 8.4
Milk	6.3 – 6.6
Saliva	6.5 – 7.5
Blood	7.3 – 7.5
Sea water	8.5
Tears	7.4

## Limitation of pH-Scale

- pH value of the solution does not give us at once idea of the relative strength of the solution.
- pH is zero for 1N solution of strong acid.
- pH is negative for concentration 2N, 3N, 10N etc for strong acids.
- At higher concentration in place of pH Hammett acidity functions are used.

## Illustrations

5. How many grams of NaOH must be dissolved in one litre of solution to give it a pH value of 11?

**Solution** Given pH of solution = 11

$$\text{pH} = -\log [\text{H}^+]$$

$$11 = -\log [\text{H}^+]$$

$$[\text{H}^+] = 10^{-11} \text{ M}$$

$$K_w = [\text{H}^+] [\text{OH}^-] = 1 \times 10^{-14}$$

$$[\text{OH}^-] = \frac{1 \times 10^{-14}}{10^{-11}} = 1 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 1 \times 10^{-3} \text{ M}$$

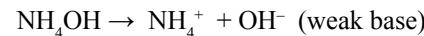
$$\text{Strength} = \text{Molarity} \times \text{mol. weight}$$

$$= 10^{-3} \times 40$$

$$= 0.04 \text{ g / litre.}$$

6. Find the pH of 0.004 M  $\text{NH}_4\text{OH}$  having 3.2 % dissociation.

## Solution



c 0 conc. before  
ionization

$c(1 - \alpha)$   $c\alpha$  conc. after  
ionization

$$[\text{H}^+] = c\alpha = 3 \times 10^{-3} \times \frac{4.3}{100}.$$

$$= 1.29 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log [1.29 \times 10^{-4}]$$

$$\text{pH} = 3.8894$$

7. Find the pH of solution obtained by mixing 20 ml of 0.1 M HCl and 30 ml of 0.2 M  $\text{H}_2\text{SO}_4$

**Solution** Milli equivalent of  $\text{H}^+$  from HCl =  $20 \times 0.1 = 2$

Milli equivalent of  $\text{H}^+$  from  $\text{H}_2\text{SO}_4$

$$= 30 \times 0.2 \times 2 = 12$$

Total milli equiv. of  $\text{H}^+$  in solution =  $2 + 12$

$$= 14$$

Total volume of solution =  $20 + 30 = 50$

$$[\text{H}^+] = \frac{M_{\text{eq}}}{V_{\text{in ml}}} = \frac{14}{50} = 0.28$$

$$\text{pH} = -\log [\text{H}^+] = -\log (0.28) = 0.5528$$

8. Calculate the pH of a solution containing 2.0 g of NaOH per litre of water.

**Solution** As the solution contains 2.0 g of NaOH per

litre of water, its normality =  $\frac{2}{40} = \frac{1}{20} \text{ N}$

$[\text{OH}^-] = 1/20 \text{ g-ion / litre}$

$$[\text{H}^+] [\text{OH}^-] = 10^{-14}$$

$$[\text{H}^+] [1/20] = 10^{-14}$$

$$[\text{H}^+] = 20 \times 10^{-14} = 2 \times 10^{-13} \text{ g ion /litre}$$

$$\text{pH} = -\log [\text{H}^+]$$

$$= -\log [2 \times 10^{-13}]$$

$$= -[\log 2 - 13 \log 10]$$

$$= -[0.3010 - 13]$$

$$= 12.699$$

9. Calculate the pH of a solution obtained by mixing 50 ml of 0.01 M  $\text{Ba}(\text{OH})_2$  solution with 50 ml water.

### Solution

$$\text{N}_1\text{V}_1 = \text{N}_2\text{V}_2$$

$\text{Ba}(\text{OH})_2$  mixture

[Normality of solution of  $\text{Ba}(\text{OH})_2 = 2 \times$  its molarity, as its mol. wt =  $2 \times$  eq. wt]

$$0.01 \times 2 \times 50 = \text{N}_2 \times (50 + 50)$$

(as it is assumed as 100% ionized).

$$\text{N}_2 = \frac{0.01 \times 100}{100} = 0.01 \text{ N}$$

$$[\text{OH}^-] = \alpha \cdot \text{N} = 1 \times 0.01 = 10^{-2}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log 10^{-2} = 2 \log 10$$

$$\text{pOH} = 2$$

$$\text{pH} + \text{pOH} = 14$$

$$\text{pH} + 2 = 14$$

$$\text{pH} = 12$$

10. A 0.100 N NaOH solution was added to 50.0 ml of 0.100 N  $\text{HC}_2\text{H}_3\text{O}_2$  solution. What would be the pH of the solution after the addition of (i) 50.0 ml of NaOH solution and (ii) 60.0 ml of NaOH solution?

### Solution

- (i) The addition of 50.00 ml of 0.100 N NaOH solution represents the end point of the titration. Therefore, the solution will be:

$$\frac{0.00500 \text{ mole } \text{NaC}_2\text{H}_3\text{O}_2}{0.100 \text{ litre solution}}$$

= 0.0500 M with respect to  $\text{NaC}_2\text{H}_3\text{O}_2$ .

$$\text{As } K_h = \frac{K_w}{K_b} = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]}$$

Suppose  $X = [\text{HC}_2\text{H}_3\text{O}_2] = [\text{OH}^-]$

Since salt is essentially 100% ionized,

$$[\text{C}_2\text{H}_3\text{O}_2^-] = 0.05 \text{ mole per litre}$$

$$K_h = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{X^2}{5.0 \times 10^{2-}}.$$

On solving,

$$X = 5.3 \times 10^{-6} \text{ mole OH}^- \text{ per litre}$$

$$\text{As } [\text{H}^+] [\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{5.3 \times 10^{-6}} = 1.9 \times 10^{-9}$$

$$\text{pH} = \log_{10} \frac{1}{1.9 \times 10^{-9}} = 8.7$$

- (ii) All  $\text{OH}^-$  ions will originate from the excess of 10.0 ml of 0.100 N NaOH, therefore

$$[\text{OH}^-] = \frac{(0.010)(0.100) \text{ mole}}{0.100 \text{ litre}}$$

$$= 9.1 \times 10^{-3} \text{ mole per litre}$$

$$\text{pOH} = \log_{10} \frac{1}{9.1 \times 10^{-3}} = 2.04$$

$$\text{pH} = 14.00 - 2.04 = 11.96$$

11. Saccharin ( $K_a = 2 \times 10^{-12}$ ) is a weak acid represented by formula  $\text{HSaC}$ . A  $4 \times 10^{-4}$  mole amount of saccharin is dissolved in 200 cm<sup>3</sup> water of pH 3. Assuming no change in volume, calculate the concentration of  $\text{Sa}^-$  ions in the resulting solution at equilibrium.

### Solution

$$[\text{HSaC}] = \frac{\text{mole}}{\text{litre}} = \frac{4 \times 10^{-4}}{200 / 1000} = 2 \times 10^{-3} \text{ M}$$

The dissociation of  $\text{HSaC}$  takes place in presence of  $[\text{H}^+] = 10^{-3}$

$$\text{HSaC} \rightleftharpoons \text{H}^+ + \text{Sa}^-$$

Conc. before disso.  $2 \times 10^{-3}$   $10^{-3}$  0

In presence of  $\text{H}^+$  the dissociation of  $\text{HSaC}$  is almost negligible because of common ion effect. So at equilibrium

$$[\text{HSaC}] = 2 \times 10^{-3}$$

$$[\text{H}^+] = 10^{-3}$$

$$K_a = \frac{[\text{H}^+][\text{Sa}^-]}{[\text{HSaC}]}$$

$$2 \times 10^{-12} = \frac{[10^{-3}][\text{Sa}^-]}{2 \times 10^{-3}}$$

$$[\text{Sa}^-] = 4 \times 10^{-12} \text{ M}$$

12. An aqueous solution contains 10% ammonia by mass and has a density of 0.99 g cm<sup>-3</sup>. Calculate hydroxyl and hydrogen ion concentration in this solution.  $K_a$  for  $\text{NH}_4^+ = 5.0 \times 10^{-10}$  M

### Solution

$$\frac{\text{Weight of NH}_3}{\text{Weight of solution}} = \frac{10}{100}.$$

As 100 g solution contains 10 g  $\text{NH}_3$ ,

$$\text{So MNH}_3 = \frac{10 \times 1000}{17 \times (100/0.99)} = 5.82$$

(as V = mass/density)



Before diss. 1 0 0

After diss.  $(1 - \alpha)$   $\alpha$   $\alpha$

$$[\text{OH}^-] = C. \alpha = C\sqrt{(K_b / C)} = \sqrt{(K_b . C)}$$

As  $C = 5.82$  M

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{5 \times 10^{-10}} = 2 \times 10^{-5}$$

$$[\text{OH}^-] = \sqrt{[2 \times 10^{-5} \times 5.82]} = 1.07 \times 10^{-2} \text{ M}$$

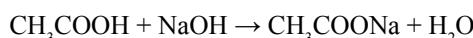
$$[\text{H}^+] = \frac{10^{-14}}{1.07 \times 10^{-2}} = 0.9268 \times 10^{-12} \text{ M}$$

$$\text{pH} = -\log_{10} [\text{H}^+] = -\log 0.9268 \times 10^{-12}$$

$$= 12.0330$$

13. Calculate the pH at the equivalence point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M NaOH.  $K_a$  for acid =  $1.9 \times 10^{-5}$ .

**Solution** Suppose V ml of acid and V ml of NaOH is used concentration of both acid and NaOH are same.



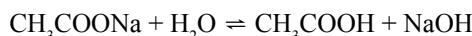
$$\text{Conc. } \frac{0.1 \times V}{2V} \quad \frac{0.1 \times V}{2V} \quad 0 \quad 0$$

before reac.

$$\text{Conc. after reaction} \quad 0 \quad 0 \quad \frac{0.1 \times V}{2V} \quad \frac{0.1 \times V}{2V}$$

reaction

$$[\text{CH}_3\text{COONa}] = \frac{0.1}{2} = 0.05 \text{ M}$$



$$[\text{OH}^-] = C \alpha = C \sqrt{(K_h / C)} = \sqrt{(K_h . C)}$$

$$= \sqrt{[(K_w / K_a) . C]}$$

$$= \frac{\sqrt{(10^{-14} \times 0.05)}}{\sqrt{(1.9 \times 10^{-5})}} = 5.12 \times 10^{-6}$$

$$\text{pOH} = 5.29$$

$$\text{pH} = 8.71$$

14. How many moles of calcium hydroxide must be dissolved to produce 250.0 ml of an aqueous solution of pH 10.65? Assume complete dissociation.

**Solution**  $\text{pH} + \text{pOH} = 14$

$$\text{pOH} = 14 - \text{pH}$$

$$= 14 - 10.65 = 3.35$$

$$-\log [\text{OH}^-] = 3.35$$

$$\log [\text{OH}^-] = -3.35 = 4.65$$

$$[\text{OH}^-] = \text{Antilog } 4.65 = 4.47 \times 10^{-4} \text{ M}$$

$$= 4.47 \times 10^{-4} \text{ mol L}^{-1}$$

Moles of  $\text{OH}^-$  required for 250 ml

$$= \frac{4.47 \times 10^{-4} \text{ mol L}^{-1}}{(250 \text{ ml} / 1000 \text{ ml})} = 1.12 \times 10^{-4} \text{ mol}$$

As 1 mol  $\text{Ca}(\text{OH})_2$  produces 2 mol  $\text{OH}^-$  ions.

So moles of  $\text{Ca}(\text{OH})_2$  dissolved

$$= \frac{1.12 \times 10^{-4} \text{ mol}}{2} = 5.6 \times 10^{-5} \text{ mol Ca}(\text{OH})_2$$

15. The pH of the 0.10 M hydrocyanic acid solutions is 5.2. What is the value of  $K_a$  for hydrocyanic acid?

**Solution**  $\text{pH} = -\log \text{H}^+ = 5.2$

$$\log [\text{H}^+] = -5.2 = 6.8$$

$$[\text{H}^+] = \text{Antilog } 6.8 = 6.31 \times 10^{-6} \text{ M}$$



$$0.1 - 6.31 \times 10^{-6} \quad 6.31 \times 10^{-6} \text{ M} \quad 6.31 \times 10^{-6} \text{ M}$$

$$= 0.1 \text{ M}$$

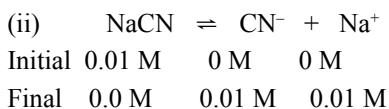
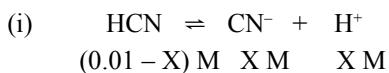
$$K_a = \frac{[\text{H}^+] [\text{CN}^-]}{[\text{HCN}]}$$

## 5.60 ■ Ionic Equilibrium

$$= \frac{(6.31 \times 10^{-6} \text{ M}) \times (6.31 \times 10^{-6} \text{ M})}{0.1 \text{ M}} \\ = 3.9816 \times 10^{-10} = 4.0 \times 10^{-10}$$

16. The concentration of HCN and NaCN in a solution is 0.01 M each. Calculate the concentration of hydrogen and hydroxyl ions if the dissociation constant of HCN is  $7.2 \times 10^{-10}$ .

### Solution



So at equilibrium,  $[\text{H}^+] = X \text{ M}$

$$[\text{CN}^-]_{\text{total}} = [\text{CN}^-]_{\text{acid}} + [\text{CN}^-]_{\text{salt}} \\ = X \text{ M} + 0.01 \text{ M} = 0.01 \text{ M}$$

$$[\text{HCN}] = 0.01 \text{ M} - X \text{ M} = 0.01 \text{ M}$$

$$\text{pH} = \text{pK}_a + \log_{10} \frac{[\text{CN}^-]}{[\text{HCN}]}$$

$$= -\log 7.2 \times 10^{-10} + \log \frac{1.01 \text{ M}}{0.01 \text{ M}}$$

$$-\log [\text{H}^+] = \log 7.2 \times 10^{-10}$$

$$[\text{H}^+] = 7.2 \times 10^{-10} \text{ M}$$

$$[\text{OH}^-] = \frac{\text{K}_w}{[\text{H}^+]}$$

$$= \frac{1 \times 10^{-14}}{7.2 \times 10^{-10}} = 1.4 \times 10^{-5} \text{ M}$$

### Buffer Solution

Buffer solution is the solution whose pH does not change much by the addition of a small amount of a strong acid or a base. It is also called reserve acidity or basicity solution as it resists change of pH value and this action to resists pH change is called Buffer action.

#### Features:

- It has a definite pH i.e., reserve acidity or basicity.
- Its pH does not change on standing for a long time also.
- Its pH does not change on dilution also.
- Its pH slightly (unnoticeable) changes by the addition of small quantity of a strong acid or base.

### Buffer Capacity

Buffer capacity is the ratio of number of moles of the acid or base added in one litre of the solution so as to change its pH by unity. It is denoted by  $\Phi$ .

$$\Phi = \frac{\text{No. of moles of acid / base added to 1 lit}}{\text{Change in pH}}$$

Or

It is also defined as the amount of a strong acid or strong base needed to change the pH of a buffer by one unit. Suppose we take a buffer solution of volume 1 L with 'q' mole of salt and 'p' mol of salt + acid. The pH of the buffer can be given as follows

$$\text{pH} = \text{pK}_a + \log \frac{q}{p-q}$$

On adding 'x' mol of a strong acid (monobasic), the pH changes to

$$\text{pH}' = \text{pK}_a + \log \frac{q-x}{(p-q+x)}$$

$$\Delta \text{pH} = \log \frac{q}{p-q} - \log \frac{q-x}{(p-q+x)}$$

$$\Delta \text{pH} = \log \left( \frac{q}{p-q} \times \frac{(p-q+x)}{(q-x)} \right)$$

$$= \frac{1}{2.303} \ln \left( \frac{q}{p-q} \times \frac{(p-q+x)}{(q-x)} \right)$$

On differentiating with respect to  $x$  we get

$$\frac{d\Delta \text{pH}}{dx} = \left( \frac{1}{\frac{q}{(p-q)} \times \left( \frac{p-q+x}{q-x} \right)} \right) \times \frac{q}{p-q}$$

$$\times \left[ \frac{(q-x) \times 1 - (p-q+x) \times (-1)}{(q-x)^2} \right] \times \frac{1}{2.303}$$

$$= \frac{p}{(p-q+x)(q-x) 2.303}$$

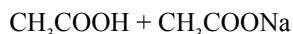
On taking the inverse

$$\frac{dx}{d\Delta \text{pH}} = \frac{(p-q+x)(q-x) 2.303}{p}$$

### Type of Buffer Solution

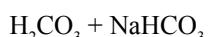
1. **Acidic Buffer:** It is a solution of a weak acid and its salt with a strong base.

Example,



Phthalic acid + potassium phthalate

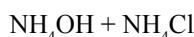
Boric acid + Borax



Citric acid + sodium citrate

- 2. Basic Buffer:** It is a solution of a weak base and its salt with a strong acid

Example,



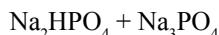
Glycine + glycine hydrogen chloride

Glycerol + glycerine hydrogen chloride

- 3. Ampholyte Solution:** Example, Protein and amino acids also act like a buffer solution.

- 4.** A mixture of acidic salt and normal salt of a polybasic acid

Example,



- 5.** Salt of weak acid and weak base (in water)

Example,



## Uses of Buffer

Some of the important uses of buffer are as follows:

- (i) To determine pH value with the help of an indicator.
- (ii)  $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$  buffer solution is used to precipitate carbonates of Vth group
- (iii)  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$  buffer is used to remove  $\text{PO}_4^{3-}$  in qualitative inorganic analysis after IIInd group.
- (iv)  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$  buffer is used to precipitate lead chromate quantitatively in gravimetric analysis.
- (v) They are also used in paper, dye, printing ink, dairy product etc.
- (iv)  $\text{H}_2\text{CO}_3 + \text{NaHCO}_3$  maintains pH of blood.

## Illustrations

- 17.** Calculate the pH of a 0.01 M  $\text{NH}_4\text{OH}$  solution containing 10 mol / litre of  $\text{NH}_4\text{Cl}$ ? ( $\text{pK}_b = 4.76$ )

**Solution** [Conjugate base] = 0.10 M  $\text{NH}_3$  in  $\text{H}_2\text{O}$

$$[\text{Conjugate acid}] = 1.0 \text{ M } \text{NH}_4^+$$

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$= 4.76 + \log \frac{1.0}{0.1}$$

$$= 4.76 + \log 10 = 5.76$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14 - 5.76 = 8.24$$

- 18.** What volume of 0.1 M sodium formate solution should be added to 50 ml of 0.05 M formic acid to produce a buffer solution of pH = 4.0;  $\text{pKa}$  of formic acid = 3.80?

**Solution** Suppose  $V$  ml of 0.1 M  $\text{HCOONa}$  is mixed to 50 ml of 0.05 M  $\text{HCOOH}$ .

$$[\text{Molarity}] = \frac{\text{Total millimole}}{\text{Total volume}}$$

$$\text{In mixture } [\text{HCOONa}] = \frac{0.1 \times V}{(V + 50)}.$$

$$[\text{HCOOH}] = \frac{50 \times 0.05}{V + 50}$$

$$\text{pH} = -\log \text{Ka} + \log \frac{[\text{Salt}]}{[\text{Acid}]}.$$

$$4.0 = 3.80 + \log_{10} \frac{(0.1 \times V)}{(V + 50)/2.5 / (V + 50)}$$

$$V = 39.62 \text{ ml}$$

- 19.** Calculate the change in pH of 1 litre buffer solution containing 0.1 mole each of  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$  up on addition of;

- (i) 0.02 mole of dissolved gaseous HCl

- (ii) 0.02 mole of dissolved NaOH.

(Assume no change in volume.  $\text{KNH}_3 = 1.8 \times 10^{-5}$ )

**Solution** Initial pH of solution when,

$$[\text{NH}_3] = \frac{0.1}{1} \text{ and } [\text{NH}_4\text{Cl}] = \frac{0.1}{1}$$

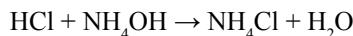
$$\text{pOH} = -\log_{10} 1.8 \times 10^{-5} + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]} .$$

$$= -\log_{10} 1.8 \times 10^{-5} + \log_{10} \frac{0.1}{0.1}$$

$$\text{pOH} = 4.7447$$

$$\text{pH} = 9.2553$$

(i) When 0.02 mole of HCl are added,



$$\text{Mole before diss. } 0.02 \quad 0.1 \quad 0.1$$

$$\text{Mole after diss. } 0 \quad 0.08 \quad (0.1 + 0.02)$$

$$\text{As} \quad \text{Volume} = 1 \text{ litre}$$

$$\text{So} \quad [\text{NH}_4\text{OH}] = 0.08 / 1$$

$$[\text{NH}_4\text{Cl}] = 0.12 / 1$$

$$\text{pOH}_1 = -\log_{10} 1.8 \times 10^{-5} + \log_{10} \frac{0.12}{0.08}$$

$$\text{pOH}_1 = 4.9208$$

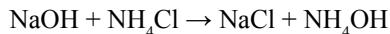
$$\text{pH}_1 = 9.0792$$

$$\text{Change in pH} = \text{pH} - \text{pH}_1 = 9.2553 - 9.0792$$

$$= +0.1761$$

Change in pH = 0.1761 unit i.e., pH decreases

(ii) When 0.02 mole of NaOH are added,



$$\text{Mole before diss. } 0.02 \quad 0.1 \quad 0 \quad 0.1$$

$$\text{Mole after diss. } 0 \quad 0.08 \quad 0.02 \quad 0.12$$

$$\text{pOH}_2 = -\log_{10} 1.8 \times 10^{-5} + \log_{10} \frac{0.08}{0.12}$$

$$\text{pOH}_2 = 4.5686$$

$$\text{pH}_2 = 9.4314$$

$$\text{Change in pH} = \text{pH} - \text{pH}_2 = 9.2553 - 9.4314$$

$$= -0.1761$$

Change in pH = 0.1761 that is, pH increases.

20. Calculate the amount of  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$  required to prepare a buffer solution of pH 9.0 when total concentration of buffering reagents is 0.6 mol litre<sup>-1</sup>.  $\text{pK}_b$  for  $\text{NH}_3 = 4.7$ ,  $\log_{10} 2 = 0.30$

**Solution**  $\text{pOH} = -\log_{10} K_b + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]} .$

$$5 = 4.7 + \log_{10} \frac{a}{b} .$$

$$a / b = 2$$

$$\text{So } a = 2b$$

$$\text{Given } a + b = 0.6$$

$$2b + b = 0.6$$

$$3b = 0.6$$

$$b = 0.2 \text{ mole}$$

$$= 0.2 \times 17 = 3.4 \text{ g/litre}$$

$$a = 0.4 \text{ mole}$$

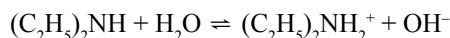
$$= 0.4 \times 53.5 = 21.4 \text{ g/litre}$$

$$[\text{Salt}] = 0.4 \text{ M}$$

$$[\text{Base}] = 0.2 \text{ M}$$

21. The pH of 0.05 M aqueous solution of diethyl amine is 12.0. Calculate  $K_b$ .

**Solution**



$$\text{Initial conc. } 1 \quad 0 \quad 0$$

$$\text{Eq. conc. } (1 - \alpha) \quad \alpha \quad \alpha$$

$$[\text{OH}^-] = C \alpha$$

Here C is conc. of base and  $C = 0.05 \text{ M}$

$$\text{As } \text{pH} = 12$$

$$\text{So } \text{pOH} = 2$$

$$[\text{OH}^-] = 10^{-2} \text{ M}$$

$$C \alpha = 10^{-2}$$

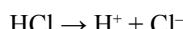
$$0.05 \times \alpha = 10^{-2} \quad (\text{as } C = 0.05)$$

$$\alpha = 0.2$$

$$K_b = \frac{C\alpha^2}{(1 - \alpha)} = \frac{0.05 \times (0.2)^2}{(1 - 0.2)}$$

$$= \frac{0.05 \times 0.04}{0.8} = 2.5 \times 10^{-3}$$

22. A solution contains 0.1 M  $\text{H}_2\text{S}$  and 0.3 M HCl. Calculate the conc. of  $\text{S}^{2-}$  and  $\text{HS}^-$  ions in solution. Given  $\text{K}_{\text{a}1}$  and  $\text{K}_{\text{a}2}$  for  $\text{H}_2\text{S}$  are  $10^{-7}$  and  $1.3 \times 10^{-13}$  respectively.

**Solution**

Due to common ion effect the dissociation of  $\text{H}_2\text{S}$  is suppressed and the  $[\text{H}^+]$  in solution is due to HCl.

$$K_{\text{a}_1} = \frac{[\text{H}^+] [\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$10^{-7} = \frac{[0.3] [\text{HS}^-]}{[0.1]} \quad [\text{as } [\text{H}^+] \text{ from HCl} = 0.3]$$

$$[\text{HS}^-] = \frac{10^{-7} \times 0.1}{0.3} = 3.3 \times 10^{-8} \text{ M}$$

$$K_{\text{a}_1} = \frac{[\text{H}^+] [\text{HS}^-]}{[\text{H}_2\text{S}]} \text{ and } K_{\text{a}_2} = \frac{[\text{H}^+] [\text{S}^{2-}]}{[\text{HS}^-]}$$

$$K_{\text{a}_1} \times K_{\text{a}_2} = \frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

$$10^{-7} \times 1.3 \times 10^{-13} = \frac{[0.3]^2 [\text{S}^{2-}]}{[0.1]}$$

$$[\text{S}^{2-}] = \frac{1.3 \times 10^{2-} \times 0.1}{0.09} = 1.44 \times 10^{-20} \text{ M}$$

23. Two buffers, (X) and (Y) of pH 4.0 and 6.0 respectively are prepared from acid HA and the salt NaA. Both the buffers are 0.50 M in HA. What would be the pH of the solution obtained by mixing equal volumes of the two buffers? ( $K_{\text{HA}} = 1.0 \times 10^{-5}$ )

**Solution**  $\text{pH} = -\log_{10} K_{\text{a}} + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]}$ .

When pH = 4

$$4 = -\log_{10} 1.0 \times 10^{-5} + \log_{10} \frac{[\text{Salt}]}{0.5 \text{ M}}$$

$$4 = 5 + \log_{10} \frac{[\text{Salt}]}{0.5 \text{ M}}$$

$$\log_{10} \frac{[\text{Salt}]}{0.5 \text{ M}} = -1$$

$$[\text{Salt}] = 0.1 \times 0.5 = 0.05 \text{ M}$$

When pH = 6,

$$6 = -\log_{10} (1.0 \times 10^{-5}) + \log_{10} \frac{[\text{Salt}]}{0.5 \text{ M}}$$

$$6 = 5 + \log_{10} \frac{[\text{Salt}]}{0.5 \text{ M}}$$

$$\log_{10} \frac{[\text{Salt}]}{0.5 \text{ M}} = 1$$

$$[\text{Salt}] = 10 \times 0.5 = 5 \text{ M}$$

Suppose V litre each of both buffers are mixed. The concentration of the salt in this solution will be:

$$[\text{Salt}] = \frac{(0.05 \text{ M} \times V) + (5 \text{ M} \times V)}{2V} = \frac{5.05}{2} \text{ M}$$

Concentration of [HA] in mixed buffer

$$= \frac{(0.5 \text{ M} \times V) \times (0.5 \text{ M} \times V)}{2V} = 0.5 \text{ M}$$

$$\text{pH} = -\log_{10} (1.0 \times 10^{-5}) + \log_{10} \frac{[5.05 / 2]}{0.5}$$

$$= 5 + 0.7033 = 5.7033$$

**Solubility**

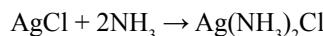
It is the weight in gm of solute present in 100 ml of solvent. It is denoted by 's' and is expressed in mol per litre or gm per litre. The number of moles of solute in 1 L of saturated solution is known as molar solubility.

Solubility  $\propto$  1/concentration of common ions  
or number of common ions

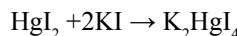
Example, The solubility of AgCl in water in presence of  $\text{AgNO}_3$ .

Solubility increases due to complex ion formation.

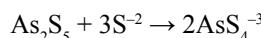
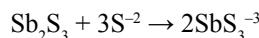
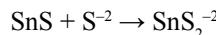
Example, AgCl has more solubility in ammonia due to complex formation.



$\text{HgCl}_2$  has more solubility in KI due to complex formation (Nesseler's reagent).



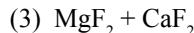
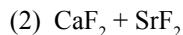
In IIInd group analysis  $\text{SnS}$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{As}_2\text{S}_3$  are soluble in  $(\text{NH}_4)_2\text{S}$  due to complex ion formation.



**Simultaneous Solubility:** It is the solubility of a solution of two electrolytes having common ions.

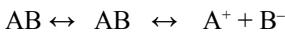
## 5.64 ■ Ionic Equilibrium

Example, (1)  $\text{AgBr} + \text{AgSCN}$



**Solubility Product:** It is the product of the molar concentrations of ions of an electrolyte in a saturated solution at a particular temperature. It is denoted by  $K_{\text{sp}}$  or  $S$ .

### For a Binary Electrolyte AB:



Solid un-ionised

$$\text{So } K = \frac{[\text{A}^+] [\text{B}^-]}{[\text{AB}]}$$

$$\text{or } K \cdot [\text{AB}] = [\text{A}^+] [\text{B}^-]$$

or

$$K_{\text{sp}} = [\text{A}^+] [\text{B}^-] \text{ At constant temp.}$$

### General Representation



$$K_{\text{sp}} = [\text{A}^{+y}]^x [\text{B}^{-x}]^y$$

Example (1)



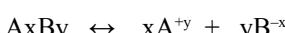
$$K_{\text{sp}} = [\text{Ca}^+]^2 [\text{F}^-]^2$$

Example (2)



$$K_{\text{sp}} = [\text{Ag}^+]^2 [\text{CrO}_4^{-2}]$$

### Relation between Solubility(s) and Solubility Product ( $K_{\text{sp}}$ )



$$\begin{array}{ccc} a & 0 & 0 \\ a-s & x s & y s \end{array}$$

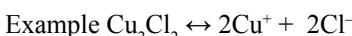
$$K_{\text{sp}} = (x s)^x \cdot (y s)^y$$

or

$$K_{\text{sp}} = x^x y^y (s)^{x+y}$$

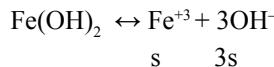
If  $\alpha$  is given

$$K_{\text{sp}} = x^x y^y (\alpha s)^{x+y}$$

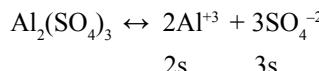


$$\begin{array}{cc} 2s & 2s \end{array}$$

$$\text{so } K_{\text{sp}} = 2^2 \cdot 2^2 \cdot (s)^{2+2} = 16 s^4$$



$$K_{\text{sp}} = 1^1 \cdot 3^3 (s)^{1+3} = 27 s^4$$



$$K_{\text{sp}} = 2^2 \cdot 3^3 \cdot (s)^{2+3} = 108 s^5$$



$$K_{\text{sp}} = 3^3 \cdot 3^3 \cdot 2^2 \cdot (s)^{3+3+2} = 2916 s^8$$

### Solubility Product and Precipitation

- If  $K_{\text{sp}} \approx$  Ionic product

Solution is saturated and for precipitation more solute is to be added.

- If Ionic product  $> K_{\text{sp}}$

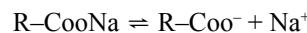
solution is super saturated so easily precipitated.

- If Ionic product  $< K_{\text{sp}}$

Solution is unsaturated so no precipitation takes place.

### Application of Solubility Product

- In the precipitation of Soap by adding a little Nacl: on adding a little Nacl soap gets precipitated as ionic product becomes more than  $K_{\text{sp}}$ .



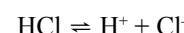
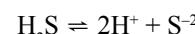
$$K_{\text{sp}} \geq [\text{R-COO}^-] [\text{Na}^+]$$

on adding Nacl

$$[\text{R-COO}^-] [\text{Na}^+] > K_{\text{sp}}$$

- In Analytical Chemistry:

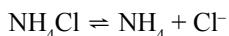
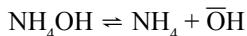
- Cation of IIInd gp.  $[\text{Cu}^{2+}, \text{Bi}^{+2}, \text{Hg}^{2+}, \text{Pb}^{2+}, \text{Cd}^{+2}]$  are precipitated as  $\text{S}^{-2}$  by using  $\text{H}_2\text{S} + \text{HCl}$  at lower lenc entrant of  $\text{S}^{-2}$  due to the tact that they have lower  $K_{\text{sp}}$  than other group cations.



Common ions

Here due to common ion effect conc<sup>n</sup> π S<sup>-2</sup> decreases so far other gp. Cations K<sub>s.p</sub> > Ionic product hence they cannot be precipitated.

- (B) Cations of IIIrd gp. (Fe<sup>3+</sup>, Al<sup>3+</sup>, Cr<sup>3+</sup>) are precipitated at low concentration of OH due to their lower K<sub>sp</sub> than other gp. Cat-ions by using NH<sub>4</sub>OH + NH<sub>4</sub>Cl.



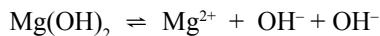
Common ions

Due to common ions conc<sup>n</sup> of OH decreases so other gp. Cations cannot be precipitated as for them k<sub>sp</sub> > Ionic product.

## Illustrations

24. The solubility of Mg(OH)<sub>2</sub> in water at 25°C is 0.00912 g per litre. Find K<sub>sp</sub> for Mg(OH)<sub>2</sub> assuming complete ionization.

### Solution



1 mole      1 mole      2 mole

$$\text{K}_{\text{sp}} = [\text{Mg}^{2+}] [\text{OH}^-]^2 \quad \dots\dots\dots (\text{i})$$

$$\begin{aligned} \text{Concentration of Mg(OH)}_2 &= \frac{0.00912 \text{ g}}{58.3 \text{ g/mole}} \\ &= 0.000156 \text{ mole per litre} \end{aligned}$$

Since one mole of Mg(OH)<sub>2</sub> yields one mole of Mg<sup>2+</sup> ion and two moles of OH<sup>-</sup> ion, then

$$[\text{Mg}^{2+}] = 0.000156 \text{ mole per litre}$$

$$[\text{OH}^-] = 2 \times 0.000156 = 0.000312 \text{ mole per litre}$$

On putting the values in equation (i)

$$\text{K}_{\text{sp}} = (0.000156) \times (0.000312)^2$$

$$= 1.52 \times 10^{-11} \text{ for Mg(OH)}_2 \text{ at } 25^\circ\text{C}$$

25. The solubility product of SrF<sub>2</sub> in water is 8 × 10<sup>-10</sup>. Find its solubility in 0.1 M NaF aqueous solution.

### Solution

For SrF<sub>2</sub>,

$$\text{K}_{\text{sp}} = [\text{Sr}^{2+}] [\text{F}^-]^2$$

Let the solubility of SrF<sub>2</sub> in 0.1 M NaF be X mol L<sup>-1</sup>.

$$8 \times 10^{-10} = (X)(2X + 0.1)^2$$

(Neglecting X<sup>2</sup> and X<sup>3</sup> terms)

$$0.01 X = 8 \times 10^{-10}$$

$$X = 8 \times 10^{-8} \text{ mol L}^{-1}$$

26. What (H<sub>3</sub>O<sup>+</sup>) must be maintained in a saturated H<sub>2</sub>S solution to precipitate Pb<sup>2+</sup>, but not Zn<sup>2+</sup> from a solution in which each ion is present at a concentration of 0.01 M?

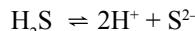
(K<sub>sp</sub> of H<sub>2</sub>S = 1.1 × 10<sup>-22</sup>, K<sub>sp</sub> of ZnS = 1.0 × 10<sup>-21</sup>)

**Solution** For ZnS not to be precipitate from a solution of Zn<sup>2+</sup> and Pb<sup>2+</sup>.

$$[\text{Zn}^{2+}] [\text{S}^{2-}] < \text{K}_{\text{sp}} \text{ of ZnS}$$

$$[10^{-2}] [\text{S}^{2-}] < 1.0 \times 10^{-21}$$

or the maximum [S<sup>2-</sup>] = 10<sup>-19</sup> at which ZnS will begin to precipitate or upto this concentration, no precipitation will occur.



$$[\text{H}^+]^2 [\text{S}^{2-}] = 1.1 \times 10^{-22}$$

$$[\text{H}^+]^2 [10^{-19}] = 1.1 \times 10^{-22}$$

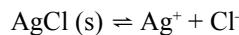
$$[\text{H}^+]^2 = 11 \times 10^{-4}$$

$$[\text{H}^+] = 3.3 \times 10^{-2} \text{ M}$$

Therefore if [H<sup>+</sup>] = 3.3 × 10<sup>-2</sup> or slightly higher, the precipitation of ZnS will not take place and only PbS will precipitate.

27. Determine the concentration of NH<sub>3</sub> solution whose one litre can dissolve 0.10 mole AgCl. K<sub>sp</sub> of AgCl and K<sub>f</sub> of Ag(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> are 1.0 × 10<sup>-10</sup> M<sup>2</sup> and 1.6 × 10<sup>7</sup> M<sup>-2</sup> respectively.

**Solution** AgCl + 2NH<sub>3</sub> ⇌ Ag(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> + Cl<sup>-</sup>



$$\text{K}_{\text{sp}} = [\text{Ag}^+] [\text{Cl}^-] \quad \dots\dots\dots (\text{i})$$

$$\text{Given} \quad \text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+$$

$$\text{K}_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+] [\text{NH}_3]^2} \quad \dots\dots\dots (\text{ii})$$

## 5.66 ■ Ionic Equilibrium

From equation (i) and (ii)

$$K_{sp} \times K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+] [\text{Cl}^-]}{[\text{NH}_3]^2}$$

$$1 \times 10^{-10} \times 1.6 \times 10^7 = \frac{a \times a}{[\text{NH}_3]^2}$$

Given: solubility of  $\text{AgCl}$  = 0.1 M

$a = 0.1 \text{ M}$  for  $\text{Ag}(\text{NH}_3)_2^+$  and  $\text{Cl}^-$

$$[\text{NH}_3]^2 = \frac{0.1 \times 0.1}{1.6 \times 10^{-3}} = 6.25$$

$$[\text{NH}_3] = 2.5 \text{ M}$$

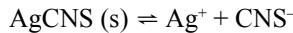
0.2 M  $\text{NH}_3$  is needed to dissolve 0.1 M  $\text{Ag}^+$  ions, so

$$[\text{NH}_3] = 2.5 + 0.2 = 2.7 \text{ M}$$

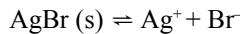
28. Calculate simultaneous solubility of  $\text{AgCNS}$  and  $\text{AgBr}$  in a solution of water.

$K_{sp}$  of  $\text{AgBr}$  =  $5 \times 10^{-13}$  and  $K_{sp}$  of  $\text{AgCNS}$  =  $1 \times 10^{-12}$ .

**Solution** Suppose solubility of  $\text{AgCNS}$  and  $\text{AgBr}$  in a solution is X and Y mol litre<sup>-1</sup> respectively.



[Ion] furnished on dissolution X X



[Ion] furnished on dissolution Y Y

$$[\text{Ag}^+] = X + Y$$

$$[\text{Br}^-] = Y$$

$$K_{sp} \text{ of } \text{AgCNS} = [\text{Ag}^+] [\text{CNS}^-]$$

$$1 \times 10^{-12} = (X + Y)(X) \quad \dots \text{(i)}$$

$$K_{sp} \text{ of } \text{AgBr} = [\text{Ag}^+] [\text{Br}^-]$$

$$5 \times 10^{-13} = (X + Y)(Y) \quad \dots \text{(ii)}$$

From equation (i) and (ii)

$$\frac{X}{Y} = \frac{10^{-12}}{5 \times 10^{-13}} = 2$$

$$X = 2Y$$

From equation (i),

$$(2Y + Y)(2Y) = 1 \times 10^{-12}$$

$$6Y^2 = 1 \times 10^{-12}$$

$$Y = 4 \times 10^{-7} \text{ mol litre}^{-1}$$

From equation (i),

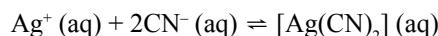
$$(X + X/2)(X) = 1 \times 10^{-12}$$

$$X = 8.16 \times 10^{-7} \text{ mole litre}^{-1}$$

29. Determine the number of mole of  $\text{AgI}$  which may be dissolved in 1.0 litre of 1.0 M  $\text{CN}^-$  solution.  $K_{sp}$  for  $\text{AgI}$  and  $K_c$  for  $\text{Ag}(\text{CN})_2^-$  are  $1.2 \times 10^{-17} \text{ M}^2$  and  $7.1 \times 10^{19} \text{ M}^{-2}$  respectively.

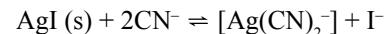
**Solution**  $\text{AgI} (\text{s}) \rightleftharpoons \text{Ag}^+ (\text{aq}) + \text{I}^- (\text{aq})$

$$K_{sp} = [\text{Ag}^+] [\text{I}^-] = 1.2 \times 10^{-17} \quad \dots \text{(i)}$$



$$K_f = \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{Ag}^+] [\text{CN}^-]^2} = 7.1 \times 10^{19} \quad \dots \text{(ii)}$$

Suppose X mole of  $\text{AgI}$  is dissolved in  $\text{CN}^-$  solution



Mole before diss. 1 0 0

Mole after reaction (1 - 2X) X X

From equation (i) and (ii),

$$K_{eq} = K_{sp} \times K_f$$

$$K_{eq} = \frac{[\text{Ag}(\text{CN})_2^-] [\text{I}^-]}{[\text{CN}^-]^2} = 1.2 \times 10^{-17} \times 7.1 \times 10^{19}$$

$$K_{eq} = 8.52 \times 10^2 \quad \dots \text{(iii)}$$

$$K_{eq} = 8.52 \times 10^2 = \frac{X \cdot X}{(1 - 2X)} = \frac{X^2}{(1 - 2X)^2}.$$

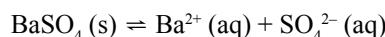
$$\frac{X}{1 - 2X} = 29.2$$

$$X = 29.2 - 58.4X$$

$$X = 0.49 \text{ mole}$$

30. The solubility product of  $\text{BaSO}_4$  is  $1.5 \times 10^{-9}$ . Find out its solubility in (i) Pure water and (ii) 0.10 M  $\text{BaCl}_2$

**Solution** (i) In pure water



As 1 mole of  $\text{BaSO}_4$  dissolves to give 1 mole of  $\text{Ba}^{2+}$  ions and 1 mole of  $\text{SO}_4^{2-}$  ions. Therefore, if  $S$  is the solubility of  $\text{BaSO}_4$  in moles per litre, then

$$\text{Solubility} = S = [\text{Ba}^{2+}] = [\text{SO}_4^{2-}]$$

$$\text{K}_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = S \times S = S^2$$

$$S = \sqrt{\text{K}_{\text{sp}}} = \sqrt{(1.5 \times 10^{-9})}$$

$$= 3.87 \times 10^{-5} \text{ mol L}^{-1}$$

(ii) In 0.1 M  $\text{BaCl}_2$ :

0.1 M  $\text{BaCl}_2$  dissolves completely to give 0.1 M  $\text{Ba}^{2+}$  (common ions) and 0.1 M  $\text{Cl}^-$  ions



$$1 \text{ mol} \quad 1 \text{ mol} \quad 2 \text{ mol}$$

$$0.1 \text{ M} \quad 0.1 \text{ M} \quad 0.2 \text{ M}$$

At equilibrium

$$[\text{Ba}^{2+}]_{\text{eq}}$$

$$= [\text{Ba}^{2+}] \text{ from } \text{BaCl}_2 \text{ added} + [\text{Ba}^{2+}] \text{ from } \text{BaSO}_4$$

$$= 0.1 \text{ M} + S \text{ M}$$

$$= 0.1 \text{ M}$$

$$[\text{SO}_4^{2-}] = S$$

$$\text{K}_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

$$[\text{SO}_4^{2-}] = S = \frac{\text{K}_{\text{sp}}}{[\text{Ba}^{2+}]}$$

$$= \frac{1.5 \times 10^{-9}}{0.1 \text{ M}} = 1.5 \times 10^{-8} \text{ M}$$

31. A solution has 0.05  $\text{Mg}^{2+}$  and 0.05 M  $\text{NH}_3$ . Calculate the concentration of  $\text{NH}_4\text{Cl}$  required to prevent the formation of  $\text{Mg}(\text{OH})_2$  in this solution.  $\text{K}_{\text{sp}}$  of  $\text{Mg}(\text{OH})_2 = 9.0 \times 10^{-12}$  and ionization constant of  $\text{NH}_3 = 1.8 \times 10^{-5}$ .

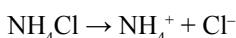
**Solution**  $\text{Mg}(\text{OH})_2(s) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$

$$\text{K}_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

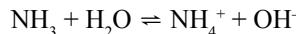
$$[\text{OH}^-]^2 = \frac{\text{K}_{\text{sp}}}{[\text{Mg}^{2+}]} = \frac{9.0 \times 10^{-12}}{0.05 \text{ M}} = 180 \times 10^{-12}$$

$$[\text{OH}^-] = \sqrt{(180 \times 10^{-12})} = 13.4 \times 10^{-6} \text{ M}$$

Therefore,  $[\text{OH}^-]$  concentration cannot be more than  $13.4 \times 10^{-6} \text{ M}$ .



$$\text{MNH}_4^+ = \text{MNH}_4\text{Cl}$$



$$\text{K}_{\text{eq}} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

$$[\text{NH}_4^+] = \frac{[\text{NH}_3] \times \text{K}_{\text{eq}}}{[\text{OH}^-]}$$

$$= \frac{0.05 \text{ M} \times 1.8 \times 10^{-5}}{13.4 \times 10^{-6}} = 0.067 \text{ M}$$

Concentration of  $\text{NH}_4\text{Cl}$  needed = 0.067 M

32. Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.05 mol  $\text{L}^{-1}$  of  $\text{NH}_4\text{OH}$  and 0.25 mol  $\text{L}^{-1}$  of  $\text{NH}_4\text{Cl}$ . Calculate the concentration of aluminium and magnesium ions in solution.

$$\text{K}_{\text{sp}} \text{ Al}(\text{OH})_3 = 6 \times 10^{-32}$$

$$K_b \text{ NH}_4\text{OH} = 1.8 \times 10^{-5}$$

$$\text{K}_{\text{sp}} \text{ Mg}(\text{OH})_2 = 6 \times 10^{-10}$$

**Solution**  $\text{pOH} = \log_{10} \frac{[\text{Salt}]}{[\text{Base}]} - \log K_b$

$$-\log_{10} [\text{OH}^-] = \log_{10} 0.25 - \log_{10} \frac{1.8 \times 10^{-5}}{0.05}$$

$$\log_{10} [\text{OH}^-] = \log_{10} \frac{1.8 \times 10^{-5}}{5}$$

$$[\text{OH}^-] = 0.36 \times 10^{-5} \text{ mol L}^{-1}$$

$$[\text{Al}^{3+}] = \frac{\text{K}_{\text{sp}} \text{ Al}(\text{OH})_3}{[\text{OH}^-]^3}$$

$$= \frac{6 \times 10^{-32}}{(0.36 \times 10^{-5})^3}.$$

$$= 1.29 \times 10^{-10} \text{ mol L}^{-1}$$

$$[\text{Mg}^{2+}] = \frac{\text{K}_{\text{sp}} \text{ Mg}(\text{OH})_2}{[\text{OH}^-]^2}$$

$$= \frac{6 \times 10^{-10}}{(0.36 \times 10^{-5})^2} = 46.3 \text{ mol L}^{-1}$$

## Salt Hydrolysis

When a salt is added in water ions of the salt interact with water to cause acidity or basicity in aqueous solution. This ionic interaction is called salt hydrolysis. Interaction of cation is cationic hydrolysis and interaction of anion is anionic hydrolysis.

## 5.68 ■ Ionic Equilibrium

- Hydrolysis is reverse of neutralization and an endothermic process.
  - If hydrolysis constant is  $K_h$  and neutralization constant is  $K_n$ .
- $$K_n = \frac{1}{K_h}$$
- A solution of the salt of strong acid and weak base is acidic and for it  $pH < 7$  or  $[H^+] > 10^{-7}$   
Example,  $FeCl_3$  (weak base + strong acid): Solution is acidic and involves cationic hydrolysis
  - A solution of the salt of strong base and weak acid is basic and for it  $pH > 7$  or  $[H^+] < 10^{-7}$   
Example,  $KCN$  (strong base + weak acid): Solution is basic and involves anionic hydrolysis.
  - A solution of the salt of weak acid and weak base –  
If  $K_a > K_b$  it is acidic  
If  $K_a < K_b$  it is basic  
If  $K_a = K_b$  it is neutral
  - $CH_3COONH_4$  (weak acid + weak base): Solution is neutral and involves both cationic and anionic hydrolysis
  - A solution of the salt of strong acid and strong base is neutral or  $pH = 7$  or  $[H^+] = 10^{-7}$
  - A salt of strong acid and strong base is never hydrolyzed however, ions are hydrated.  
Example,  $K_2SO_4$  (however, strong base + strong acid)

**Degree of Hydrolysis:** It is the amount or fraction of the salt which is hydrolysed. It is denoted by  $h$ .

$$h = \frac{\text{No. of moles of salt hydrolysed}}{\text{Total moles of the salt taken}}$$

### Various Expressions for $K_h$ , $h$ and $pH$ for Different Type of Salts:

1. For the salt of weak acid and strong base ( $KCN$ )

$$K_h = \frac{K_w}{K_a}$$

$$h = \sqrt{(K_h / C)}$$

$$h = \sqrt{(K_w / K_a \cdot C)}$$

$$pH = \frac{1}{2} [pK_w + pK_a + \log C]$$

$$pOH = \frac{1}{2} [pK_w - pK_a - \log C]$$

2. For the salt of strong acid and weak base ( $FeCl_3$ )

$$K_h = \frac{K_w}{K_b}$$

$$h = \sqrt{(K_h / C)}$$

$$h = \sqrt{(K_w / K_b \cdot C)}$$

$$pH = \frac{1}{2} [pK_w - pK_b - \log C]$$

3. For the salt of weak acid and weak base ( $NH_4Cn$ )

$$K_h = \frac{K_w}{K_a K_b}$$

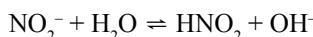
$$h = \sqrt{(K_w / K_a \cdot K_b)}$$

$$pH = \frac{1}{2} [pK_w + pK_a - pK_b]$$

### Illustrations

33. Calculate hydrolysis constant of salt containing  $NO_2^-$  ion. Given the  $K_a$  for  $HNO_2 = 4.5 \times 10^{-10}$ .

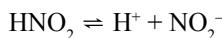
**Solution**  $NO_2^-$  ion hydrolysis as



$$K_h = \frac{[HNO_2][OH^-]}{[NO_2^-]} \quad \dots \dots (1)$$

$$K_w = [H^+][OH^-] \quad \dots \dots (2)$$

$HNO_2$  ionizes as follows:



$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]} \quad \dots \dots (3)$$

From equations (1) and (3)

$$K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{45 \times 10^{-10}} \cdot$$

$$= 2.22 \times 10^{-5}$$

34. Calculate for 0.01 N solution of sodium acetate,

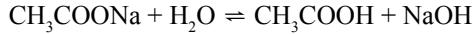
a. Hydrolysis constant

b. Degree of hydrolysis

c. pH

Given  $K_a = 1.9$

### Solution



Before hydrolysis 1 0 0

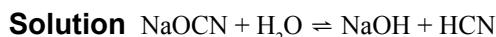
After hydrolysis  $(1 - \alpha)$   $\alpha$   $\alpha$

$$(a) K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.9 \times 10^{-5}} = 5.26 \times 10^{-10}$$

$$(b) \alpha = \sqrt{(K_h / C)} = \frac{\sqrt{(5.26 \times 10^{-10})}}{\sqrt{0.01}} = 2.29 \times 10^{-4}$$

$$(c) [\text{OH}^-] \text{ from NaOH, a strong alkali} = C\alpha \\ = 0.01 \times 2.29 \times 10^{-4} \\ = 2.29 \times 10^{-6} \text{ M} \\ \text{pOH} = 5.64 \\ \text{pH} = 8.36$$

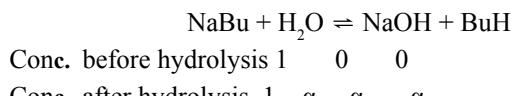
35. Calculate the percentage hydrolysis in 0.003 M aqueous solution of NaOCN. Ka for HOCN =  $3.33 \times 10^{-4}$ .



$$\alpha = \sqrt{(K_h / C)} = \frac{\sqrt{K_w}}{\sqrt{(K_a \cdot C)}} \\ = \frac{\sqrt{(10^{-14})}}{\sqrt{(3.33 \times 10^{-4} \times 0.003)}} \\ h = 10^{-4} \\ \% \text{ hydrolysis} = 10^{-4} \times 100 = 10^{-2}$$

36. Ka for butyric acid is  $2.0 \times 10^{-5}$ . Calculate pH and hydroxyl ion concentration in 0.2 M aqueous solution of sodium butyrate.

**Solution**



$$[\text{OH}^-] = C \alpha = C \cdot \sqrt{(K_h / C)} = \sqrt{(K_h \cdot C)} \\ = \sqrt{(K_w / K_a) \cdot C}$$

$$[\text{OH}^-] = \frac{10^{-14} \times 0.2}{2 \times 10^{-5}} = \sqrt{10^{-10}} = 10^{-5}$$

$$\text{pOH} = 5$$

$$\text{pH} + \text{pOH} = 14$$

$$\text{So } \text{pH} = 14 - 5 = 9$$

37. Ka for ascorbic acid (HAsC) is  $5 \times 10^{-5}$ . Calculate the hydrogen ion concentration and percentage

of hydrolysis in an aqueous solution in which the concentration of AsC<sup>-</sup> ions is 0.02 M.



$$[\text{OH}^-] = C \alpha = C \cdot \sqrt{(K_h / C)} = \sqrt{(K_h \cdot C)} \\ = \sqrt{(K_w / K_a) \cdot C}$$

$$= \frac{\sqrt{(10^{-14} \times 0.02)}}{\sqrt{(5 \times 10^{-5})}} = 2 \times 10^{-6}$$

$$[\text{H}^+] = \frac{1 \times 10^{-14}}{2 \times 10^{-6}} = 5 \times 10^{-9}$$

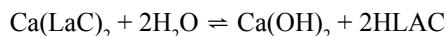
$$\alpha = \sqrt{(K_h / C)} = \frac{\sqrt{K_w}}{\sqrt{(K_a \cdot C)}} .$$

$$= \frac{\sqrt{10^{-14}}}{\sqrt{(5 \times 10^{-5} \times 0.02)}} = 10^{-4}$$

$$= 0.01 \%$$

38. Calcium lactate is a salt of weak acid and represented as  $\text{Ca}(\text{LaC})_2$ . A saturated solution of  $\text{Ca}(\text{LaC})_2$  contains 0.13 mole of salt in 0.50 litre solution. The pOH of this 5.60. Assuming complete dissociation of salt, calculate Ka of lactic acid.

**Solution**



$$\begin{array}{ccc} \text{Before hydrolysis} & 1 & 0 \\ \text{After hydrolysis} & (1 - \alpha) & \alpha & \alpha \end{array}$$

$$[\text{Ca}(\text{LaC})_2] = \frac{0.13}{0.5} = 0.26 \text{ M}$$

$$[\text{LaC}] = 0.26 \times 2 = 0.52 \text{ M}$$

(as 1 mole  $\text{Ca}(\text{LaC})_2$  gives 2 mole LaC.)

$$[\text{OH}^-] = C \alpha = C \cdot \sqrt{(K_h / C)} = \sqrt{(K_h \cdot C)}$$

$$= \frac{\sqrt{(K_w \times C)}}{\sqrt{K_a}}$$

Here C is the concentration of anion which undergoes hydrolysis

$$10^{-5.60} = \frac{\sqrt{(10^{-14} \times 0.52)}}{\sqrt{K_a}}$$

$$K_a = 8.25 \times 10^{-4}$$

## ACID AND BASES

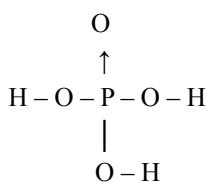
### Arrhenius Concept of Acid and Base

According to it “Acids are H<sup>+</sup> ion donor in water and bases are OH<sup>-</sup> ion donor in water”.

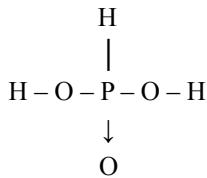
#### 1. Acid:

- HA + H<sub>2</sub>O → A<sup>-</sup> + H<sub>3</sub>O<sup>+</sup> Hydronium ion or Hydrated proton
- Water can accept H<sup>+</sup> to form hydronium ion (H<sub>3</sub>O<sup>+</sup>) due to hydrogen bonding.  
Example, – [H<sub>5</sub>O<sub>2</sub><sup>+</sup>, H<sub>7</sub>O<sub>3</sub><sup>+</sup>]
- H<sup>+</sup> can hold water molecule by hydrogen bond as it has high heat of hydration.  
Example, – HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HX
- H<sub>3</sub>O<sup>+</sup> has sp<sup>3</sup> hybridization and trigonal pyramidal shape.
- Number of H<sup>+</sup> donated = Basicity or protosity of the acid  
Example,

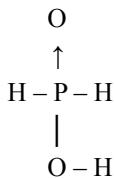
#### 1. H<sub>3</sub>PO<sub>4</sub> (tribasic)



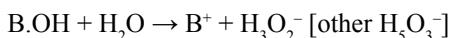
#### 2. H<sub>3</sub>PO<sub>3</sub> (dibasic)



#### 3. H<sub>3</sub>PO<sub>2</sub>



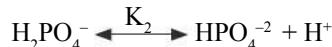
#### 2. Base:



Example, NaOH, KOH etc.

### Strength of Acid and Base

- Acidic strength  $\propto K_a$   
Dissociation const. of acid
- Base strength  $\propto K_b$   
Dissociation const. of base
- Relative strength =  $\sqrt{(K_1 / K_2)}$



Here K<sub>1</sub> > K<sub>2</sub> >> K<sub>3</sub> so the correct acidic strength order is



- As negative charge develops the removal of H<sup>+</sup> becomes more and more difficult so acidic nature decreases.

### REMEMBER

This concept fails to explain acidic and basic nature in case of AlCl<sub>3</sub>, BX<sub>3</sub>, NH<sub>3</sub> etc.

### Bronsted Lowry Concept or Proton Concept

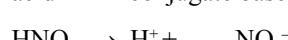
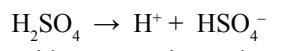
- 1. **Acid:** Acids are Proton or H<sup>+</sup> donor.



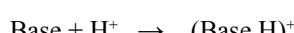
Acid conjugate base



Conjugate base



- 2. **Base:** Bases are proton or H<sup>+</sup> acceptor.



or proton conjugate base

given by acid



Base conjugate acid



## 5.72 ■ Ionic Equilibrium

Some multiple bonded molecules which form complexes with transition metals. Example, CO, NO, C<sub>2</sub>H<sub>4</sub> etc.

### Strength of Lewis Base

Lewis base  $\propto$  1 / Electronegativity difference

Example,



Less electronegativity difference

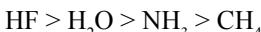
### REMEMBER

CO, RCH = CH<sub>2</sub>, RC ≡ CH are border line Lewis bases.

### Factors Effecting Acidic Strength:

- Acidic strength  $\propto$  Electronegativity difference

Example (1)



As electronegativity of F > O > N > C



As electronegativity of N > C > B

Example (2)

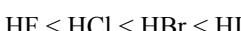


As electronegativity of Cl > Br > I.

- Acidic strength  $\propto$  Size of central atom

or easy removal of H<sup>+</sup>

Example,



- Strength of oxyacids  $\propto$  Oxidation

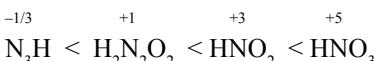
number of central atom

Example (1)



Increasing order of acidic nature

Example (2)



### REMEMBER

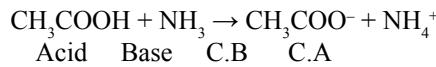
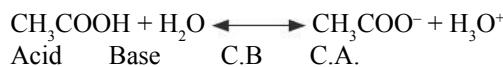


**Effect of Solvent on Acidic Strength:** A solvent also effects acidic strength and it is called leveling effects.

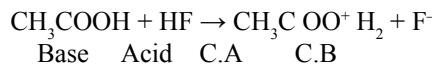
Example (1) – CH<sub>3</sub>COOH

CH<sub>3</sub>COOH behaves like a weak acid in water but in liquid ammonia it is a strong acid as ammonia has more tendency than water to accept H<sup>+</sup>.

Example,



CH<sub>3</sub>COOH in HF behaves like a base as HF is stronger acid than it.



Example (2) – HNO<sub>3</sub>

HNO<sub>3</sub> is although a strong acid in water but a weak acid in CH<sub>3</sub>COOH and a base in HF.

- HClO<sub>4</sub> (the strongest acid) becomes a weak acid in HF.

### Some important acids in the decreasing order of acidic strength:

HClO<sub>4</sub>, HClO<sub>3</sub>, HI, H<sub>2</sub>SO<sub>4</sub>, HBr, HCl, H<sub>3</sub>O<sup>+</sup>, HNO<sub>3</sub>, HF, HSO<sub>4</sub><sup>-</sup>, H<sub>3</sub>PO<sub>4</sub>, HCOOH, CH<sub>3</sub>COOH, H<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>S, NH<sub>4</sub><sup>+</sup>, HCN, C<sub>6</sub>H<sub>5</sub>OH, H<sub>2</sub>O, R – OH, HC ≡ CH, NH<sub>3</sub>, H<sub>2</sub>C = CH<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>12</sub> (Cyclo hexane)

The strength of conjugate base will be in increasing order for the above acidic strength order that is,

ClO<sub>4</sub><sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, I<sup>-</sup>, H<sub>2</sub>O, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HCOO<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, HS<sup>-</sup>, NH<sub>3</sub><sup>-</sup>, CN<sup>-</sup>, C<sub>6</sub>H<sub>5</sub>O<sup>-</sup>, OH<sup>-</sup>, OR<sup>-</sup>, C ≡ CH<sup>-</sup>, NH<sub>2</sub><sup>-</sup>, CH = CH<sub>2</sub><sup>-</sup>, CH<sub>3</sub><sup>-</sup>, C<sub>2</sub>H<sub>5</sub><sup>-</sup>, C<sub>6</sub>H<sub>11</sub><sup>-</sup>,

### Enhance Your Knowledge

- According to Ingold concept an electrophile is an acid while a nucleophile is a base.

Example,  $\text{AlCl}_3$  (El) is an acid and  $\text{NH}_3$  (Nu) is a base.

- In the reaction  $\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-$  the lewis base is  $\text{I}^-$ .
- $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{H}_2\text{O} \rightarrow [\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+} + \text{H}_3\text{O}^+$   
Acid      Base      C.B.      C.A.

- $[\text{Zn}(\text{H}_2\text{O})_5\text{OH}]^{2+} + \text{H}_3\text{O}^+ \rightarrow [\text{Zn}(\text{H}_2\text{O})_6]^{3+} + \text{H}_2\text{O}$   
Base      Acid      C.A.      C.B.
- The reaction of a cation or anion with water accompanied by cleavage of O – H bond is called salt hydrolysis.

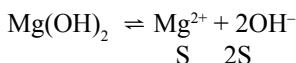
## Solved Problems from the IITs

- The solubility of  $\text{Mg}(\text{OH})_2$  in pure water is  $9.57 \times 10^{-3} \text{ g L}^{-1}$ . Calculate its solubility in  $\text{g L}^{-1}$  in 0.02 M  $\text{Mg}(\text{NO}_3)_2$  solution.

[IIT 1986]

**Solution** Solubility of  $\text{Mg}(\text{OH})_2$  in pure water

$$\begin{aligned} &= 9.57 \times 10^{-3} \text{ g L}^{-1} \\ &= \frac{9.57 \times 10^{-3}}{\text{Mol. mass}} \text{ mol L}^{-1} \\ &= \frac{9.57 \times 10^{-3}}{58} = 1.65 \times 10^{-4} \text{ mol L}^{-1} \end{aligned}$$



$$\begin{aligned} K_s &= [\text{Mg}^{2+}][\text{OH}^-]^2 \\ &= S \times (2S)^2 = 4S^3 \\ &= 4 \times (1.65 \times 10^{-4})^3 \\ &= 17.9685 \times 10^{-12} \end{aligned}$$

Let  $S'$  be the solubility of  $\text{Mg}(\text{OH})_2$  in presence of  $\text{Mg}(\text{NO}_3)_2$ .

$$\text{As } [\text{Mg}^{2+}] = (S' + c) = (S' + 0.02)$$

$$[\text{OH}^-] = 2S'$$

$$\text{So } K_s = (S' + 0.02)(2S')^2$$

$$17.9685 \times 10^{-12} = 4(S')^2(S' + 0.02)$$

$$\frac{17.9685 \times 10^{-12}}{4} = (S')^3 + 0.02(S')^2$$

On neglecting  $(S')^3$  we get,

$$4.4921 \times 10^{-12} = 0.02(S')^2$$

$$(S')^2 = \frac{4.4921}{0.02} \times 10^{-12}$$

$$S' = 14.9868 \times 10^{-6} \text{ mol L}^{-1}$$

$$\begin{aligned} \text{Solubility of } \text{Mg}(\text{OH})_2 \text{ in } \text{g L}^{-1} &= S' \times M \\ &= 14.9868 \times 10^{-6} \times 58 \\ &= 8.69 \times 10^{-4} \text{ g L}^{-1} \end{aligned}$$

- What is the pH of the solution when 0.2 mole of hydrochloric acid is added to one litre of a solution containing 1 M acetic acid and acetate ion? Assume that the total volume is one litre.  $K_a$  for  $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$ .

[IIT 1987]

**Solution** On adding HCl, the free hydrogen ions combine with  $\text{CH}_3\text{COO}^-$  ions to form  $\text{CH}_3\text{COOH}$ . Thus, the concentration of acetic acid increases while that of  $\text{CH}_3\text{COO}^-$  ions decreases.

$$[\text{CH}_3\text{COOH}] = (0.2 + 1) = 1.2 \text{ mol litre}^{-1}$$

$$[\text{Salt}] = (1 - 0.2) = 0.8 \text{ mol litre}^{-1}$$

According to Henderson's equation

$$\text{pH} = \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

$$= \log_{10} \frac{0.8}{1.2} - \log_{10} 1.8 \times 10^{-5}$$

$$= \log_{10} 2 - \log_{10} 3 - \log_{10} 1.8 \times 10^{-5}$$

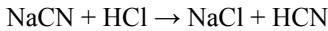
$$= 4.5687$$

- How many gram moles of HCl will be required to prepare one litre of a buffer solution (having  $\text{NaCN}$  and  $\text{HCN}$ ) of pH 8.5 using 0.01 g formula mass of  $\text{NaCN}$ ?  $K_a$  for  $\text{HCN} = 4.1 \times 10^{-10}$ ?

[IIT 1988]

**Solution** Let 'X' moles of HCl be added. It combines with  $\text{NaCN}$  to form  $\text{HCN}$ .

## 5.74 ■ Ionic Equilibrium



$$[\text{NaCN}] = (0.01 - X)$$

$$[\text{HCN}] = X$$

$$\text{pH} = \log_{10} \frac{[\text{NaCN}]}{[\text{HCN}]} - \log_{10} K_a$$

$$8.5 = \log_{10} \frac{0.01 - X}{X} - \log_{10} 4.1 \times 10^{-10}$$

$$\log_{10} \frac{(0.01 - X)}{X} = 8.5 + 0.6127 - 10.0$$

$$\frac{(0.01 - X)}{X} = 0.1296$$

$$X = \frac{0.01}{1.1296} = 0.0089 \text{ mole}$$

4. Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing  $0.05 \text{ mol L}^{-1}$  of  $\text{NH}_4\text{OH}$  and  $0.25 \text{ mol L}^{-1}$  of  $\text{NH}_4\text{Cl}$ . Calculate the concentration of aluminium and magnesium ions in solution.

$$K_{\text{sp}} \text{ Al(OH)}_3 = 6 \times 10^{-32}$$

$$K_b \text{ NH}_4\text{OH} = 1.8 \times 10^{-5}$$

$$K_{\text{sp}} \text{ Mg(OH)}_2 = 6 \times 10^{-10}$$

[IIT 1989]

**Solution**  $\text{pOH} = \log_{10} \frac{[\text{Salt}]}{[\text{Base}]} - \log K_b$

$$-\log_{10} [\text{OH}^-] = \log_{10} \frac{0.25}{0.05} - \log_{10} 1.8 \times 10^{-5}$$

$$\log_{10} [\text{OH}^-] = \log_{10} \frac{1.8 \times 10^{-5}}{5}$$

$$[\text{OH}^-] = 0.36 \times 10^{-5} \text{ mol L}^{-1}$$

$$[\text{Al}^{3+}] = \frac{K_{\text{sp}} \text{ Al(OH)}_3}{[\text{OH}^-]^3}$$

$$= \frac{6 \times 10^{-32}}{(0.36 \times 10^{-5})^3}$$

$$= 1.29 \times 10^{-10} \text{ mol L}^{-1}$$

$$[\text{Mg}^{2+}] = \frac{K_{\text{sp}} \text{ Mg(OH)}_2}{[\text{OH}^-]^2}$$

$$= \frac{6 \times 10^{-10}}{(0.36 \times 10^{-5})^2} = 46.3 \text{ mol L}^{-1}$$

5. What is the pH of a  $1.0 \text{ M}$  solution of acetic acid? To what volume of one litre of this solution be diluted so that the pH of the resulting solution will be twice the original value? Given  $K_a = 1.8 \times 10^{-5}$ .

[IIT 1990]

**Solution** As degree of dissociation ( $\alpha$ ) =  $\sqrt{(K_a/C)}$

$$= \sqrt{(1.8 \times 10^{-5} / 1)}$$

$$= 4.2426 \times 10^{-3}$$

$$[\text{H}^+] = C \times \alpha$$

$$= 1 \times 4.2426 \times 10^{-3}$$

$$= 4.2426 \times 10^{-3} \text{ mol L}^{-1}$$

$$\text{pH} = -\log_{10} [\text{H}^+]$$

$$= -\log_{10} 4.2426 \times 10^{-3}$$

$$= 2.3724$$

So pH of the acetic acid solution after dilution

$$= 2 \times 2.3724 = 4.7448$$

$$\text{New } [\text{H}^+] = 10^{-4.7448} = 1.8 \times 10^{-5}$$

Suppose the new concentration is  $C_0$ .

$$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$$

$$\text{At. eq. } C_0 - 1.8 \times 10^{-5} \quad 1.8 \times 10^{-5} \quad 1.8 \times 10^{-5}$$

$$\text{As } K_a = \frac{[\text{H}^+] [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$= \frac{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}{(C_0 - 1.8 \times 10^{-5})} = 1.8 \times 10^{-5}$$

$$\text{So } C_0 = 3.6 \times 10^{-5}$$

Suppose the new volume is  $V$  litre.

$$1 \times 1 = 3.6 \times 10^{-5} \times V$$

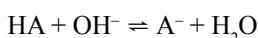
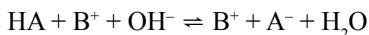
$$V = \frac{1}{3.6 \times 10^{-5}} = 2.78 \times 10^4 \text{ litre}$$

6. A certain weak acid has  $K_a = 1.0 \times 10^{-4}$ . Calculate the equilibrium constant for its reaction with a strong base.

[IIT 1991]

**Solution**  $\text{HA} + \text{BOH} \rightleftharpoons \text{BA} + \text{H}_2\text{O}$

Weak Strong



$$K = \frac{[\text{A}^-]}{[\text{HA}][\text{OH}^-]}.$$

For the following reaction,

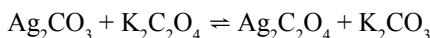
$$K_h = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

$$\text{So } K = \frac{1}{K_h}.$$

$$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.0 \times 10^{-4}} = 10^{-10}$$

$$K = \frac{1}{10^{-10}} = 10^{10}$$

7. The solubility product of  $\text{Ag}_2\text{C}_2\text{O}_4$  at  $25^\circ\text{C}$  is  $1.29 \times 10^{-11} \text{ mol}^3 \text{ L}^{-3}$ . A solution of  $\text{K}_2\text{C}_2\text{O}_4$  containing 0.1520 mole in 500 ml of water is shaken with excess of  $\text{Ag}_2\text{CO}_3$  till the following equilibrium is reached.



At equilibrium, the solution contains 0.0358 mole of  $\text{K}_2\text{CO}_3$ . Assuming the degree of dissociation of  $\text{K}_2\text{C}_2\text{O}_4$  and  $\text{K}_2\text{CO}_3$  to be equal, calculate the solubility product of  $\text{Ag}_2\text{CO}_3$ .

[IIT 1991]

**Solution**  $\text{Ag}_2\text{CO}_3 + \text{K}_2\text{C}_2\text{O}_4 \rightleftharpoons \text{Ag}_2\text{C}_2\text{O}_4 + \text{K}_2\text{CO}_3$

$$\begin{array}{lll} \text{Initial} & 0.1520 \text{ mole} & 0 \\ \text{At. eq.} & (0.1520 - 0.0358) & 0.0358 \\ & = 0.1162 \text{ mole} & \text{mole} \\ \text{Conc.} & 2 \times 0.1162 & 2 \times 0.0358 \\ & = 0.2324 \text{ M} & = 0.0716 \text{ M} \end{array}$$

$$K_{\text{sp}} \text{Ag}_2\text{C}_2\text{O}_4 = [\text{Ag}^+]^2 [\text{C}_2\text{O}_4^{2-}]$$

$$[\text{Ag}^+] = [\text{Ksp Ag}_2\text{C}_2\text{O}_4 / [\text{C}_2\text{O}_4^{2-}]]^{1/2}$$

$$K_{\text{sp}} \text{Ag}_2\text{CO}_3 = [\text{Ag}^+]^2 [\text{CO}_3^{2-}]$$

$$[\text{Ag}^+] = [\text{Ksp Ag}_2\text{CO}_3 / [\text{CO}_3^{2-}]]^{1/2}$$

$$\text{so } [\text{Ksp Ag}_2\text{C}_2\text{O}_4 / [\text{C}_2\text{O}_4^{2-}]]^{1/2}$$

$$= [\text{Ksp Ag}_2\text{CO}_3 / [\text{CO}_3^{2-}]]^{1/2}$$

$$K_{\text{sp}} \text{Ag}_2\text{CO}_3 = \frac{\text{Ksp Ag}_2\text{C}_2\text{O}_4 \times [\text{CO}_3^{2-}]}{[\text{C}_2\text{O}_4^{2-}]}$$

$$= \text{Ksp Ag}_2\text{C}_2\text{O}_4 \frac{[\text{K}_2\text{CO}_3]}{[\text{K}_2\text{C}_2\text{O}_4]}.$$

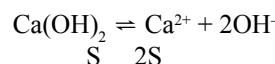
$$= 1.29 \times 10^{-11} \times \frac{0.0716}{0.2324}$$

$$= 3.97 \times 10^{-12} \text{ mol}^3 \text{ L}^{-3}$$

8. The  $K_{\text{sp}}$  of  $\text{Ca}(\text{OH})_2$  is  $4.42 \times 10^{-5}$  at  $25^\circ\text{C}$ . 500 ml of saturated solution of  $\text{Ca}(\text{OH})_2$  is mixed with equal volume of 0.4 M NaOH. How much  $\text{Ca}(\text{OH})_2$  in mg is precipitated?

[IIT 1992]

**Solution** Suppose 'S' is the solubility of  $\text{Ca}(\text{OH})_2$  in saturated solution.



$$\text{Ksp Ca}(\text{OH})_2 = [\text{Ca}^{2+}][\text{OH}^-]^2$$

$$4.42 \times 10^{-5} = S \times 4S^2$$

$$4.42 \times 10^{-5} = 4S^3$$

$$S = 0.0223 \text{ mol L}^{-1}$$

After mixing the two solutions, the total volume becomes one litre.

$$[\text{Ca}^{2+}] = \frac{0.0223}{1000} \times 500 = 0.01115 \text{ mol L}^{-1}$$

$$[\text{OH}^-] = \frac{0.0223 \times 2 \times 500}{1000} + \frac{0.4 \times 500}{1000}$$

$$[\text{From (Ca(OH)}_2] [\text{From NaOH}]$$

$$= 0.2223 \text{ mol L}^{-1}$$

Under the high concentration of  $\text{OH}^-$  ions, some  $\text{Ca}(\text{OH})_2$  will be precipitated.

$$[\text{Ca}^{2+}]_{\text{left}} [\text{OH}^-]^2 = \text{Ksp}$$

$$[\text{Ca}^{2+}]_{\text{left}} = \frac{4.42 \times 10^{-5}}{(0.2223)^2}$$

$$= 8.94 \times 10^{-4} \text{ mol L}^{-1}$$

Moles of  $\text{Ca}(\text{OH})_2$  precipitated

= Moles of  $\text{Ca}^{2+}$  precipitate

$$= [\text{Ca}^{2+}]_{\text{initial}} - [\text{Ca}^{2+}]_{\text{left}}$$

$$= 0.01115 - 8.94 \times 10^{-4}$$

$$= 111.5 \times 10^{-4} \times 8.94 \times 10^{-4}$$

## 5.76 ■ Ionic Equilibrium

$$\begin{aligned} &= 102.56 \times 10^{-4} \text{ M} = 102.56 \times 10^{-4} \times 74 \text{ g} \\ &= 7589.44 \times 10^{-4} \text{ g} \\ &= 758.944 \text{ mg} \end{aligned}$$

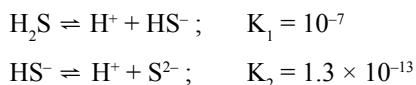
9. An aqueous solution of metal bromide,  $\text{MBr}_2$  ( $0.05 \text{ M}$ ) is saturated with  $\text{H}_2\text{S}$ . What is the minimum pH at which  $\text{MS}$  will precipitate?  $K_{\text{sp}}$  for  $\text{MS} = 6.0 \times 10^{-21}$ , concentration of saturated  $\text{H}_2\text{S} = 0.1 \text{ M}$ . ( $K_1 = 10^{-7}$  and  $K_2 = 1.3 \times 10^{-13}$  for  $\text{H}_2\text{S}$ ).

[IIT 1993]

**Solution** Minimum concentration of  $\text{S}^{2-}$  ions required to precipitate  $\text{MS}$  is

$$\begin{aligned} [\text{S}^{2-}] &= \frac{\text{K}_{\text{sp}} \text{ MS}}{[\text{M}^{2+}]} \\ &= \frac{6.0 \times 10^{-21}}{0.05} = 1.2 \times 10^{-19} \text{ M} \end{aligned}$$

$\text{H}_2\text{S}$  ionizes in solution in following steps:



$$\text{As } K_1 = \frac{[\text{H}^+] [\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$K_2 = \frac{[\text{H}^+] [\text{S}^{2-}]}{[\text{HS}^-]}$$

$$\text{So } K_1 K_2 = \frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

$$\begin{aligned} [\text{H}^+]^2 &= \frac{K_1 K_2 [\text{H}_2\text{S}]}{[\text{S}^{2-}]} \\ &= \frac{10^{-7} \times 1.3 \times 10^{-13} \times 0.1}{1.2 \times 10^{-19}} \\ &= 1.08 \times 10^{-2} \end{aligned}$$

$$[\text{H}^+] = 1.04 \times 10^{-1}$$

$$\text{pH} = -\log_{10} [\text{H}^+]$$

$$= -\log_{10} (1.04 \times 10^{-1})$$

$$= 0.98$$

10. The pH of blood stream is maintained by a proper balance of  $\text{H}_2\text{CO}_3$  and  $\text{NaHCO}_3$  concentrations. What volume of 5 M  $\text{NaHCO}_3$  solution should be mixed with a 10 ml sample of blood which is

2 M in  $\text{H}_2\text{CO}_3$ , in order to maintain a pH of 7.47?  $\text{Ka}$  for  $\text{H}_2\text{CO}_3$  in blood is  $7.8 \times 10^{-7}$ .

[IIT 1993]

**Solution** Suppose  $V$  ml of 5 M  $\text{NaHCO}_3$  solution be mixed.

$$\text{Total volume} = (V + 10) \text{ ml}$$

Concentration of  $\text{H}_2\text{CO}_3$  in the solution becomes

$$[\text{NaHCO}_3] = \frac{5 \times V}{(V + 10)} \text{ M}$$

$$[\text{H}_2\text{CO}_3] = \frac{2 \times 10}{(V + 10)} \text{ M}$$

According to Henderson's equation,

$$\text{pH} = -\log_{10} \text{Ka} + \log_{10} \frac{[\text{NaHCO}_3]}{[\text{H}_2\text{CO}_3]}$$

$$7.4 = -\log_{10} 7.8 \times 10^{-7} + \log_{10} \frac{5 \times V}{(V + 10)} \times \frac{(V + 10)}{2 \times 10}$$

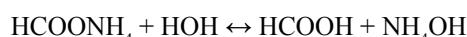
$$= -\log_{10} 7.8 \times 10^{-7} + \log_{10} \frac{V}{4}$$

$$\log_{10} \frac{V}{4} = 7.4 + \log_{10} 7.8 \times 10^{-7}$$

$$V = 78.32 \text{ ml}$$

11. Find the pH of an aqueous solution of 1.0 M ammonium formed assuming complete dissociation. ( $\text{pKa}$  of formic acid = 3.8 and  $\text{pK}_b$  of  $\text{NH}_3 = 4.8$ .)

[IIT 1995]



pH for a salt of weak acid and weak base

$$\text{pH} = \frac{1}{2} [\log_{10} K_b - \log_{10} \text{Ka} - \log \text{Kw}]$$

$$= \frac{1}{2} [\text{pKa} + \text{pKw} - \text{pK}_b]$$

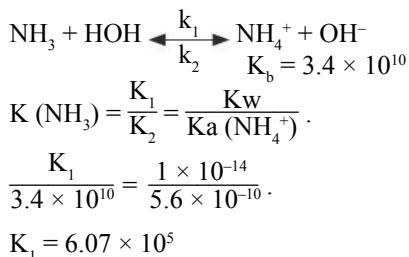
$$= \frac{1}{2} [3.8 + 14 - 4.8]$$

$$= 6.5.$$

12. The ionization constant of  $\text{NH}_4^+$  in water is  $5.6 \times 10^{-10}$  at  $25^\circ\text{C}$ . The rate constant for the reaction of  $\text{NH}_4^+$  and  $\text{OH}^-$  to form  $\text{NH}_3$  and  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$  is  $3.4 \times 10^{-10}$  litre mol $^{-1}$  sec $^{-1}$ . Find the rate constant for proton transfer from water to  $\text{NH}_3$ .

[IIT 1996]





13. For 0.50 M aqueous solution of sodium cyanide, ( $pK_b$  of  $\text{CN}^-$  is 4.70), calculate (i) hydrolysis constant (ii) degree of hydrolysis (iii) pH

[IIT 1996]

**Solution**

$$(i) K_h = \frac{K_w}{K_a} = \frac{K_w \times K_b}{K_w}$$

(As  $K_a \times K_b = K_w$ )

$$\text{So } K_h = K_b = 2 \times 10^{-5}$$

$$(ii) h = \sqrt{(K_h / c)} = \sqrt{(2 \times 10^{-5} / 0.5)} \\ = 6.3 \times 10^{-3}$$

$$(iii) [\text{OH}^-] = ch = 0.5 \times 6.3 \times 10^{-3}$$

$$[\text{OH}^-] = 3.15 \times 10^{-3}$$

$$\text{pOH} = 2.5$$

$$\text{pH} = 14 - 2.5 = 11.5$$

14. What is the pH of a 0.5 M aqueous  $\text{NaCN}$  solution?  $pK_b$  of  $\text{CN}^-$  is 4.70.

[IIT 1996]

$$\text{Solution } \text{pH} = \frac{1}{2} \text{pK}_w + \frac{1}{2} \text{pK}_a + \frac{1}{2} \log_{10} M$$

$$\text{pK}_a + \text{pK}_b = 14$$

$$\text{pK}_a + 4.7 = 14$$

$$\text{pK}_a = 9.3$$

$$\text{pH} = \frac{1}{2} \times 14 + \frac{1}{2} \times 9.3 + \frac{1}{2} \times \log_{10} 0.5 \\ = 7 + 4.65 - 0.15 \\ = 11.5$$

15. An acid type indicator,  $\text{HIn}$  differs in colour from its conjugate base ( $\text{In}^-$ ). The human eye is sensitive to colour differences only when the ratio  $[\text{In}^-] / [\text{HIn}]$  is greater than 10 or smaller than 0.1 what would be the minimum change in

pH of the solution to observe a complete colour change ( $K_a = 1.0 \times 10^{-5}$ )?

[IIT 1997]

- Solution** pH of the two given acidic buffers is as follows:

$$\text{pH} = \text{pKa} + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]}.$$

$$\text{Case I: } \text{pH} = -\log_{10} 1 \times 10^{-5} + \log_{10} 10 \\ = 5 + 1 = 6$$

$$\text{Case II: } \text{pH} = -\log_{10} 1 \times 10^{-5} + \log_{10} 0.1 \\ = 5 - 1 = 4$$

So the minimum change in pH = 6 - 4 = 2

16. What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH = 2) is mixed with 300 ml of an aqueous solution of NaOH (pH = 12)?

[IIT 1998]

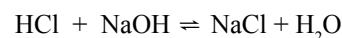
**Solution**

$$\text{As pH of HCl} = 2$$

$$\text{So } [\text{HCl}] = 10^{-2} \text{ M}$$

$$\text{pH of NaOH} = 12$$

$$[\text{NaOH}] = 10^{-2} \text{ M}$$



$$M_{eq} \quad 0 \quad 100 \times 10^{-2}$$

after reaction = 1

$$[\text{OH}^-] \text{ after reaction} = \frac{1}{500}.$$

$$= 2 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log_{10} [\text{OH}^-]$$

$$= -\log_{10} 2 \times 10^{-3} = 2.7$$

$$\text{pH} = 14 - 2.7 = 11.3$$

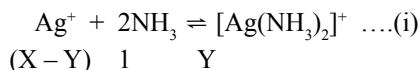
17. Given  $\text{Ag}(\text{NH}_3)_2^+ \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3$ ,

$K_c = 6.2 \times 10^{-8}$  and  $K_{sp}$  of  $\text{AgCl}$  is  $1.8 \times 10^{-10}$  at 298 K. Calculate concentration of the complex in 1 M aqueous ammonia.

[IIT 1998]

**Solution**  $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$

On adding ammonia solution, complex formation takes place.



Here

X = Solubility of AgCl in NH<sub>3</sub>

Y = Amount of complex formed

$$\text{K}_{\text{sp}} \text{ of AgCl} = [\text{Ag}^+] [\text{Cl}^-]$$

$$1.8 \times 10^{-10} = (\text{X} - \text{Y}) \cdot \text{X} \quad \dots\dots(\text{ii})$$

K<sub>c</sub> for equation (i)

$$= \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+] [\text{NH}_3]^2} \cdot$$

$$\frac{1}{6.2 \times 10^{-8}} = \frac{\text{Y}}{(\text{X} - \text{Y}) \times 1} \quad \dots\dots(\text{iii})$$

On solving equation (ii) and (iii), we obtain

$$\text{Y} = 0.0539 \text{ M.}$$

18. The solubility of Pb(OH)<sub>2</sub> in water is  $6.7 \times 10^{-6}$  M. Calculate the solubility of Pb(OH)<sub>2</sub> in a buffer solution of pH = 8.

[IIT 1999]

**Solution**  $\text{Pb}(\text{OH})_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{OH}^-$

$$\text{K}_{\text{sp}} = [\text{Pb}^{2+}] [\text{OH}^-]^2$$

$$= 6.7 \times 10^{-6} \times (2 \times 6.7 \times 10^{-6})^2$$

$$= 4 \times (6.7 \times 10^{-6})^3$$

$$= 1.2 \times 10^{-15}$$

Solubility of Pb(OH)<sub>2</sub> in buffer system of pH 8.

pH of buffer solution = 8

$$\text{pOH} = 6$$

$$[\text{OH}^-] = 10^{-6}$$

$$[\text{Pb}^{2+}] = \frac{1.2 \times 10^{-15}}{(10^{-6})^2} = 1.2 \times 10^{-3} \text{ M}$$

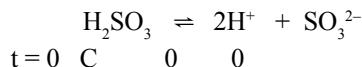
19. The average concentration of SO<sub>2</sub> in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO<sub>2</sub> in water at 298

K is 1.3653 mol litre<sup>-1</sup> and the pKa of H<sub>2</sub>SO<sub>3</sub> is 1.92, estimate the pH of rain on that day.

[IIT 2000]

**Solution**  $\text{pKa} = 1.92$

$$\text{Ka} = \text{Antilog}(-1.92) = 0.012$$



$$\text{Ka} = \frac{[\text{H}^+]^2 [\text{SO}_3^{2-}]}{[\text{H}_2\text{SO}_3]}$$

$$0.012 = \frac{(2\text{Ca})^2 \times \text{Ca}}{\text{C}(1 - \alpha)} = \frac{4\text{C}^2 \alpha^3}{(1 - \alpha)} = 4\text{C}^2 \alpha^3$$

$$0.012 = 4 \times (1.3653)^2 \times \alpha^3$$

$$\alpha = 0.117$$

$$[\text{H}^+] = 2\text{Ca}$$

$$= 2 \times 1.3653 \times 0.117$$

$$= 0.3194$$

$$\text{pH} = -\log_{10} 0.3194$$

$$= 0.495$$

20. 500 ml of 0.2 M aqueous solution of acetic acid is mixed with 500 ml of 0.2 M HCl at 25°C.

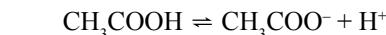
(a) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.

(b) If 6g of NaOH is added to the above solution, determine final pH. Assume there is no change in volume on mixing. Ka for acetic acid is  $1.75 \times 10^{-5}$  M.

[IIT 2002]

**Solution**

(a) Concentration of HCl and CH<sub>3</sub>COOH after mixing will be 0.1 M.



$$\text{t} = 0 \quad 0.1 \quad 0 \quad 0.1 \text{ (from HCl)}$$

$$\text{t}_{\text{eq}} \quad 0.1 - \text{X} \quad \text{X} \quad 0.1 + \text{X}$$

$$\text{Ka} = \frac{[\text{CH}_3\text{COO}^-] [\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$1.75 \times 10^{-5} = \frac{X \times (0.1 + X)}{(0.1 - X)}$$

On solving, we get

$$X = 1.75 \times 10^{-5}$$

$$[\text{H}^+] = 0.1 + X = 0.1 \text{ M}$$

$$\text{pH} = -\log_{10} [0.1] = 1$$

Degree of dissociation of acetic acid

$$= \frac{1.75 \times 10^{-5}}{0.1} = 1.75 \times 10^{-4}$$

$$(b) \text{ Number of moles of NaOH added} = \frac{6}{40} \\ = 0.15$$

$\text{CH}_3\text{COOH} + \text{HCl} + \text{NaOH} \rightleftharpoons$			
t = 0	0.1	0.1	0.15
0.05	0	0	

$\text{CH}_3\text{COONa} + \text{NaCl} + \text{H}_2\text{O}$			
0	0	0	
0.05	0	0	

$$\text{pH} = \text{pKa} + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]} \\ = -\log_{10} 1.75 \times 10^{-5} + \log_{10} \frac{0.05}{0.05} \\ = 4.757$$

21. Will the pH of water be same at 4°C and 25°C? Explain.

[IIT 2003]

### Solution

$$K_w = [\text{H}^+] [\text{OH}^-]$$

$$\text{At } 25^\circ\text{C} \quad [\text{H}^+] = [\text{OH}^-] = 1.01 \times 10^{-7} \text{ M}$$

$$\text{pH} = -\log_{10} [\text{H}^+]$$

$$= -\log_{10} [10^{-7}] = 7$$

At 4°C, ionization of water will be less than that at 25°C.

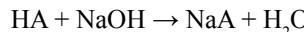
As at 25°C  $K_w = [\text{H}^+] [\text{OH}^-]$  will be less than  $10^{-14}$  so pH of water will be more than 7 at 4°C.

22. 0.1 M NaOH is titrated with 0.1 M HA till the end point;  $K_a$  for HA is  $5.6 \times 10^{-6}$  and degree

of hydrolysis is less compared to one. Calculate pH of the resulting solution at the end point.

[IIT 2004]

**Solution** Neutralization of HA with NaOH may be given as,



Concentration of salt will be 0.1 / 2 M that is, 0.05 M, as volume will be double. pH of salt after hydrolysis may be calculated as,

$$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C] \quad \dots \dots (i)$$

$$\text{p}K_w = 14$$

$$\text{p}K_a = -\log_{10} K_a$$

$$= -\log_{10} (5.6 \times 10^{-6}) = 5.2518$$

$$\log_{10} C = \log_{10} 0.05 = -1.3010$$

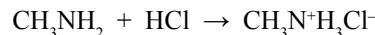
On putting the values of  $\text{p}K_w$ ,  $\text{p}K_a$  and  $\log_{10} C$  in equation (i), we obtain

$$\text{pH} = \frac{1}{2} [14 + 5.2518 - 1.3010] \\ = 8.9754$$

23. 0.1 mol of methyl amine ( $K_b = 5 \times 10^{-4}$ ) is mixed with 0.08 mol of HCl and the solution is diluted to 1 litre. Determine the hydrogen ion concentration of the resulting solution.

[IIT 2005]

### Solution



Initially 0.1 mol 0.08 mol 0 mol

On 0.02 mol 0 mol 0.08 mol

completion

This resulting solution is a basic buffer for which

$$\text{pOH} = \text{p}K_b + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]}$$

$$= -\log_{10} 5 \times 10^{-4} + \log_{10} \frac{0.08}{0.02}$$

$$= 3.3 + 0.6 = 3.9$$

$$\text{pH} = 14 - 3.9 = 10.1$$

$$\text{H}^+ = 8 \times 10^{-11} \text{ M}$$

## MULTIPLE-CHOICE QUESTIONS

### Straight Objective Type Questions (Single Choice only)

1. At 90°C, pure water has  $[H_3O^+]$   $10^{-6}$  mole litre $^{-1}$ . What is the value of  $K_w$  at 90°C?
    - a.  $10^{-8}$
    - b.  $10^{-6}$
    - c.  $10^{-12}$
    - d.  $10^{-14}$
  2. Which of the following has the highest pH ?
    - a. 0.1 M NaOH
    - b. 0.1 M  $CH_3COOH$
    - c. 0.01 M NaOH
    - d. 0.1 M HCl
  3. Which among the following is the least soluble?
    - a. MnS ( $K_{sp} = 7 \times 10^{-16}$ )
    - b. FeS ( $K_{sp} = 4 \times 10^{-19}$ )
    - c. PtS ( $K_{sp} = 8 \times 10^{-73}$ )
    - d. NiS ( $K_{sp} = 3 \times 10^{-12}$ )
  4. Of the given anions, the strongest bronsted base is
    - a.  $ClO_4^-$
    - b.  $ClO_3^-$
    - c.  $ClO_2^-$
    - d.  $ClO^-$
  5. The conjugate acid of  $O^{2-}$  ion is
    - a.  $H_2O$
    - b.  $H^+$
    - c.  $H_3O^+$
    - d.  $OH^-$
  6. The pH of a  $10^{-8}$  molar solution of HCl in water is
    - a. -8
    - b. 8
    - c. between 6 and 7
    - d. between 7 and 8
  7. An acidic buffer solution can be prepared by mixing the solutions of
    - a. sodium chloride and sodium hydroxide
    - b. sulphuric acid and sodium sulphate
    - c. ammonium chloride and ammonium hydroxide
    - d. ammonium acetate and acetic acid
  8. At 25°C, the pH of pure water is 7. It dissociates as  $H_2O(l) + H_2O(l) \leftrightarrow H_3O^+ + OH^-$ ,  $\Delta H^\circ = -13.7$  Kcal mol $^{-1}$ . pH water of 37°C is expected to be
    - a.  $> 7$
    - b. = 7
    - c.  $< 7$
    - d. none of these
- 
9. Molten sodium chloride conducts electricity due to the presence of
    - a. free ions
    - b. free molecules
    - c. free electrons
    - d. atoms of sodium and chlorine
  10. Conjugate base of hydrazoic acid is
    - a.  $HN_3^-$
    - b.  $N_2^-$
    - c. Azide ion
    - d. Nitride ion
  11. The precipitate of  $CaF_2$  ( $K_{sp} = 1.7 \times 10^{-10}$ ) is obtained when equal volumes of the following are mixed
    - a.  $10^{-2}$  M  $Ca^{2+} + 10^{-3}$  M  $F^-$
    - b.  $10^{-3}$  M  $Ca^{2+} + 10^{-5}$  M  $F^-$
    - c.  $10^{-4}$  M  $Ca^{2+} + 10^{-4}$  M  $F^-$
    - d.  $10^{-5}$  M  $Ca^{2+} + 10^{-3}$  M  $F^-$
  12. Out of  $Ca^{2+}$ ,  $Al^{3+}$ ,  $Cr^{3+}$ ,  $Mg^{2+}$  and  $Zn^{2+}$ , the reagents  $NH_4Cl$  and aqueous  $NH_3$  will precipitate
    - a.  $Ca^{2+}, Al^{3+}$
    - b.  $Al^{3+}, Cr^{3+}$
    - c.  $Bi^{3+}, Mg^{2+}$
    - d.  $Mg^{2+}, Zn^{2+}$
  13. A certain weak acid has a dissociation constant of  $1.0 \times 10^{-4}$ . the equilibrium constant for its reaction with a strong base is
    - a.  $1.0 \times 10^{10}$
    - b.  $1.0 \times 10^{14}$
    - c.  $1.0 \times 10^{-10}$
    - d.  $1.0 \times 10^{-4}$
  14. Which of the following compounds can form a buffer solution?
    - a.  $Na_2HPO_4$  and  $NaH_2PO_4$
    - b.  $HCl$  and  $NH_4Cl$
    - c.  $CH_3COOH$  and  $HCOOH$
    - d.  $Na_3PO_4$  and  $NaOH$
  15. The compound that is not a Lewis acid is
    - a.  $SnCl_4$
    - b.  $BeCl_2$
    - c.  $BF_3$
    - d.  $AlCl_3$
  16. 10 ml of 0.2 M acid is added to 250 ml of a buffer solution with pH = 6.34. The pH of the solution becomes 6.32. The buffer capacity of the solution is
    - a. 0.4
    - b. 0.3
    - c. 0.2
    - d. 0.1

17. The conjugate acid of  $\text{NH}_2^-$  is  
 a.  $\text{NH}_4^+$       b.  $\text{NH}_3$   
 c.  $\text{NH}_2\text{OH}$       d.  $\text{N}_2\text{H}_4$
18. The solubility products of  $\text{Al}(\text{OH})_3$  and  $\text{Zn}(\text{OH})_2$  are  $8.5 \times 10^{-23}$  and  $1.8 \times 10^{-14}$  respectively. If  $\text{NH}_4\text{OH}$  is added to a solution containing  $\text{Al}^{3+}$  and  $\text{Zn}^{2+}$  ions, then substance precipitated that is  
 a.  $\text{Zn}(\text{OH})_2$       b.  $\text{Al}(\text{OH})_3$   
 c. both (a) and (b)      d. none of these
19. The best indicator for detection of end point in titration of a weak acid and a strong base is  
 a. methyl red (5 to 6)  
 b. methyl orange (3 to 4)  
 c. phenolphthaleine (8 to 9.6)  
 d. bromothymol blue (6 to 7.5)
20. The pKa of acetylsalicylic acid (aspirin) is  $3.5 \times 10^{-5}$ . The pH of gastric juice in human stomach is about 2 – 3 and the pH in the small intestine is about 8. Aspirin will be  
 a. ionized to the stomach and almost unionized in the small intestine  
 b. ionized in the small intestine and almost unionized in the stomach  
 c. unionized in small intestine and in the stomach  
 d. completely ionized in the small intestine and in the stomach
21. The pKa of acetyl salicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2 – 3 and pH in the small intestine is about 8. Aspirin will be  
 a. ionized in the small intestine and almost unionized in the stomach  
 b. unionized in the small intestine and in the stomach  
 c. completely ionized in the small intestine and in the stomach.  
 d. ionized in the stomach and almost unionized in the small intestine.
22. The aqueous solution of  $\text{NH}_4\text{CN}$  is slightly alkaline because  
 a. it is a salt  
 b.  $\text{CN}^-$  ion hydrolyses to a greater extent than  $\text{NH}_4^+$  ion.  
 c.  $\text{NH}_4^+$  ion hydrolyses to a greater extent than  $\text{CN}^-$  ion.  
 d. both hydrolyses to an equal extent
23. The compound whose 0.1 M solution is basic is  
 a. ammonium acetate  
 b. ammonium sulphate
24. Which among the following acts as a basic buffer?  
 a.  $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$   
 b.  $\text{NaCl} + \text{NaOH}$   
 c.  $\text{NH}_4\text{Cl} + \text{CH}_3\text{COOH}$   
 d.  $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH}$
25. Amongst the following hydroxides, the one which has the lowest value of  $K_{\text{sp}}$  at ordinary temperature (about 25°C) is  
 a.  $\text{Mg}(\text{OH})_2$       b.  $\text{Ca}(\text{OH})_2$   
 c.  $\text{Ba}(\text{OH})_2$       d.  $\text{Be}(\text{OH})_2$
26. The strongest Bronsted base among the following ions is  
 a.  $\text{CH}_3\text{O}^-$       b.  $\text{C}_2\text{H}_5\text{O}^-$   
 c.  $(\text{CH}_3)_2\text{CHO}^-$       d.  $(\text{CH}_3)_3\text{CO}^-$
27. The pH of the neutralization point of 0.1 N ammonium hydroxide with 0.1 NHCl is  
 a. 1      b. 6  
 c. 9      d. 7
28. The following reactions are known to occur in the body  
 $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$   
 If  $\text{CO}_2$  escapes from the system  
 a. pH will decrease  
 b. Hydrogen ion concentration will diminish  
 c.  $\text{H}_2\text{CO}_3$  concentration will remain unchanged  
 d. the forward reaction will be favoured.
29. The following equilibrium is established when hydrogen chloride is dissolved in acetic acid.  
 $\text{HCl} + \text{CH}_3\text{COOH} \leftrightarrow \text{Cl}^- + \text{CH}_3\text{COOH}_2^+$   
 The set that characterizes the conjugate acid base pair is  
 a.  $(\text{HCl}, \text{CH}_3\text{COOH})$  and  $(\text{CH}_3\text{COOH}_2^+, \text{Cl}^-)$   
 b.  $(\text{HCl}, \text{CH}_3\text{COOH}_2^+)$  and  $(\text{HCl}, \text{CH}_3\text{COOH}_2^+)$  and  $(\text{CH}_3\text{COOH}, \text{Cl}^-)$   
 c.  $(\text{CH}_3\text{COOH}_2^+, \text{HCl})$  and  $(\text{Cl}^-, \text{CH}_3\text{COOH})$   
 d.  $(\text{HCl}, \text{Cl}^-)$  and  $(\text{CH}_3\text{COOH}_2^+, \text{CH}_3\text{COOH})$
30. Which of the following are Lewis acids?  
 (i)  $\text{BF}_3$       (ii)  $\text{H}_2\text{O}$   
 (iii)  $\text{HSO}_4^-$       (iv)  $\text{SO}_3$   
 a. (i) and (iii)      b. (i) and (ii)  
 c. (i) and (iv)      d. (iii) and (iv)

## 5.82 ■ Ionic Equilibrium

31. The pKa pf HCN is 9.30. The pH of a solution prepared by mixing 2.5 moles of KCN and 2.5 moles of HCN in water and making up the total volume to 500 ml is  
 a. 9.30      b. 8.30  
 c. 7.30      d. 10.30
32. What is the pH of a 0.25 M weak acid that is 2.2 % ionazied ?  
 a. 0.60      b. 2.00  
 c. 1.00      d. 2.26
33. Fear or excitement, generally causes one to breathe rapidly and it results in the decrease of  $\text{CO}_2$  concentration in blood. In what way will it change the pH of blood?  
 a. pH will increase  
 b. pH will decrease  
 c. no change  
 d. pH will adjust to 7.
34. Which of the following is correct order of increasing acidity?  
 a.  $\text{HI} < \text{HBr} > \text{HCl} < \text{HF}$   
 b.  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$   
 c.  $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$   
 d.  $\text{HF} > \text{HCl} < \text{HBr} > \text{HI}$
35. The pH of a 0.1 M aqueous solution of a weak acid (HA) is 3. What is its degree of dissociation?  
 a. 1%      b. 10%  
 c. 50%      d. 25%
36. Ammonium cyanide is a salt of  $\text{NH}_4\text{OH}$  of  $K_b = 2.5 \times 10^{-5}$  and HCN of  $K_a = 4.0 \times 10^{-10}$ . The hydrolysis constant of  $\text{NH}_4\text{CN}$  at 25°C is  
 a. 4.6      b. 4.4  
 c. 2.4      d. 1.4
37. If the acids HA and HB have dissociation constants  $1 \times 10^{-3}$  and  $1 \times 10^{-5}$  respectively, then  
 a. HA is five times stronger than HB  
 b. HA is ten times stronger than HB  
 c. HA is ten times weaker than HB  
 d. HA is five times weaker than HB
38. The dissociation constant of two acids  $\text{HA}_1$  and  $\text{HA}_2$  are  $3.0 \times 10^{-4}$  and  $1.8 \times 10^{-5}$  respectively. The relative strengths of the acids is  
 a. 1:16      b. 1:4  
 c. 4:1      d. 16:1
39. The strongest Bronsted base in the following anion is  
 a.  $\text{ClO}^-$       b.  $\text{ClO}_2^-$   
 c.  $\text{ClO}_3^-$       d.  $\text{ClO}_4^-$
40. When solid potassium cyanide is added in water, then its  
 a. pH will decrease  
 b. pH will increase  
 c. electrical conductivity will not change  
 d. pH will remain the same
41. The solubility of CuBr is  $2 \times 10^{-4}$  mol L<sup>-1</sup> at 25°C. The  $K_{\text{sp}}$  value for CuBr is  
 a.  $4 \times 10^{-6}$       b.  $4 \times 10^{-16}$   
 c.  $4 \times 10^{-11}$       d.  $4 \times 10^{-8}$
42. The solubility of  $\text{MX}_2$  type electrolyte is  $0.5 \times 10^{-4}$  mol L<sup>-1</sup>. The value of  $K_{\text{sp}}$  of the electrolyte is  
 a.  $1.35 \times 10^{-13}$       b.  $25 \times 10^{-10}$   
 c.  $5 \times 10^{-13}$       d.  $5 \times 10^{-18}$
43. The solubility product of  $\text{PbCl}_2$  at 20°C is  $1.5 \times 10^{-4}$ . Its solubility is  
 a.  $3.45 \times 10^2$  mol L<sup>-1</sup>      b.  $3.34 \times 10^4$  mol L<sup>-1</sup>  
 c.  $3.34 \times 10^{-2}$  mol L<sup>-1</sup>      d.  $3.85 \times 10^{-4}$  mol L<sup>-1</sup>
44. Which has highest pH?  
 a.  $\text{CH}_3\text{COOK}$       b.  $\text{Na}_2\text{CO}_3$   
 c.  $\text{NH}_4\text{Cl}$       d.  $\text{NaNO}_3$
45. How do you differentiate between  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  in group III?  
 a. By increasing  $\text{NH}_4^+$  ion concentration  
 b. By decreasing  $\text{OH}^-$  ion concentration  
 c. By taking excess of  $\text{NH}_4\text{OH}$   
 d. Both (a) and (b)
46. 0.005 M acid solution has 5 pH. The percentage ionization of acid is  
 a. 0.8 %      b. 0.6 %  
 c. 0.4 %      d. 0.2 %
47. Which one of the following order of acid strengths is correct?  
 a.  $\text{RCOOH} > \text{HC} \equiv \text{CH} > \text{HOH} > \text{ROH}$   
 b.  $\text{RCOOH} > \text{HOH} > \text{HC} \equiv \text{CH} > \text{ROH}$   
 c.  $\text{RCOOH} > \text{ROH} > \text{HOH} > \text{HC} \equiv \text{CH}$   
 d.  $\text{RCOOH} > \text{HOH} > \text{ROH} > \text{HC} \equiv \text{CH}$
48. The concentrations of  $\text{H}^+$  and  $\text{OH}^-$  of a 0.1 aqueous solution of 2% ionized weak acid are [ionic product of water =  $1 \times 10^{-14}$ ]  
 a.  $3 \times 10^{-2}$  M and  $5 \times 10^{-13}$  M  
 b.  $0.1 \times 10^{-3}$  M and  $3 \times 10^{-11}$  M

- c.  $0.2 \times 10^{-3}$  M and  $5 \times 10^{-11}$  M  
d.  $2 \times 10^{-3}$  M and  $5 \times 10^{-12}$  M
- 49.** When rain is accompanied by thunderstorm, the collected rain water will have a pH value
  - slightly lower than that of rain water without thunderstorm
  - which depends on the amount of dust in air
  - slightly higher than that of rain water without thunderstorm
  - uninfluenced by the occurrence of thunderstorm
- 50.** The pH value of an acid is 5 and its concentration is 1 M. What is the value of  $K_a$  for the acid?
  - $10^{-5}$
  - $10^{-10}$
  - $10^{-7}$
  - $10^{-8}$
- 51.** Which of the following is not a buffer solution?
  - 0.05 M  $\text{KClO}_4$  + 0.05 M  $\text{HClO}_4$
  - 2 M  $\text{C}_6\text{H}_5\text{NH}_2$  + 2 M  $\text{C}_6\text{H}_5^+\text{NH}_3\text{Br}$
  - 0.8 M  $\text{H}_2\text{S}$  + 0.8 M KHS
  - 3 M  $\text{H}_2\text{CO}_3$  + 3 M  $\text{KHCO}_3$
- 52.** The conjugate base of  $\text{H}_2\text{PO}_4^-$  is
  - $\text{HPO}_4^{2-}$
  - $\text{H}_3\text{PO}_4$
  - $\text{PO}_4^{3-}$
  - $\text{P}_2\text{O}_5$
- 53.** A rapid change of pH near stoichiometric point of an acid-base titration is the basis of indicator detection. The pH of solution is related to the ratio of concentrations of conjugate acid [ $\text{HIn}$ ] and base forms of the indicator by the expression
  - $\log \frac{[\text{In}^-]}{[\text{HIn}]} = \text{pH} - \text{pK}_{\text{In}}$
  - $\log \frac{[\text{HIn}^-]}{[\text{In}]} = \text{pH} - \text{pK}_{\text{In}}$
  - $\log \frac{[\text{HIn}^-]}{[\text{In}]} = \text{pK}_{\text{In}} - \text{pH}$
  - $\log \frac{[\text{In}^-]}{[\text{HIn}]} = \text{pK}_{\text{In}} - \text{pH}$
- 54.** Two solutions A and B are prepared by adding NaOH and HCl acid into water respectively. The ionic product of water will
  - increase in B and decrease in A
  - increase in A and B
  - remain the same in two solutions
  - increase in A and decrease in B
- 55.** Dimethyl glyoxime gives a red precipitate with  $\text{Ni}^{2+}$ , which is used for its detection. To get this precipitate readily, the best pH range is
  - 0.1
  - 2.3
  - 9.11
  - 3.6
- 56.** The molar solubility of a sparingly soluble salt  $\text{MX}_4$  is 'S'. The corresponding solubility product is  $K_{\text{sp}}$ . The value of 'S' is given in terms of  $K_{\text{sp}}$  by the relation
  - $S = (K_{\text{sp}} / 128)^{1/4}$
  - $S = (256 K_{\text{sp}})^{1/5}$
  - $S = (K_{\text{sp}} / 256)^{1/5}$
  - $S = (128 K_{\text{sp}})^{1/5}$
- 57.** The conjugate base of  $\text{OH}^-$  is
  - $\text{H}_2\text{O}$
  - $\text{O}^{2-}$
  - $\text{O}^-$
  - $\text{O}_2$
- 58.** What is the correct relationship between the pHs of isomolar solutions of sodium oxide ( $\text{pH}_1$ ), sodium sulphide ( $\text{pH}_2$ ), sodium selenide ( $\text{pH}_3$ ) and sodium telluride ( $\text{pH}_4$ )?
  - $\text{pH}_1 > \text{pH}_2 \approx \text{pH}_3 > \text{pH}_4$
  - $\text{pH}_1 < \text{pH}_2 < \text{pH}_3 < \text{pH}_4$
  - $\text{pH}_1 < \text{pH}_2 < \text{pH}_3 \approx \text{pH}_4$
  - $\text{pH}_1 > \text{pH}_2 > \text{pH}_3 > \text{pH}_4$
- 59.** When 10 mL of 0.1 M acetic acid ( $\text{pK}_a = 5.0$ ) is titrated against 10 mL of 0.1 M ammonia solution ( $\text{pK}_b = 5.0$ ) the equivalence point occurs at pH
  - 5.0
  - 6.0
  - 9.0
  - 7.0
- 60.**  $\text{H}_2\text{S}$  gas when passed through a solution of cations containing HCl precipitates the cations of second group of qualitative analysis but not those belonging to the fourth group. It is because
  - Solubility product of group II sulphides is more than that of group IV sulphides
  - Presence of HCl increases the sulphide ion concentration
  - Sulphides of group IV cations are unstable in HCl.
  - Presence of HCl decreases the sulphide ion concentration
- 61.** A solution has  $\text{pH} = 5$ , it is diluted 100 times, then it will become:
  - Neutral
  - More acidic
  - Basic
  - Unaffected
- 62.** A buffer solution has equal volume of 0.2 M  $\text{NH}_4\text{OH}$  and 0.02 M  $\text{NH}_4\text{Cl}$ . The  $\text{pK}_b$  of the base is 5. The pH is
  - 4
  - 10
  - 7
  - 9
- 63.** Solubility product of a salt AB is  $1 \times 10^{-8}$   $\text{M}^2$  in a solution in which the concentration of  $\text{A}^+$  ion is  $10^{-3}$

## 5.84 ■ Ionic Equilibrium

M. The salt will precipitate when the concentration of  $B^-$  ion is kept

- a.  $< 10^{-8}$  M
- b.  $> 10^{-5}$  M
- c. Between  $10^{-8}$  M to  $10^{-7}$  M
- d. Between  $10^{-7}$  M to  $10^{-6}$  M

64. Choose the correct order arranged in decreasing order of basicity.

- a.  $\text{OH}^- > \text{CH}_3\text{O}^- > \text{CH} \equiv \text{C}^-$
- b.  $\text{CH} \equiv \text{C}^- > \text{CH}_3\text{O}^- > \text{OH}^-$
- c.  $\text{CH}_3\text{O}^- > \text{OH}^- > \text{CH} \equiv \text{C}^-$
- d.  $\text{CH}_3\text{O}^- > \text{CH} \equiv \text{C}^- > \text{OH}^-$

65. In a saturated solution of the sparingly soluble strong electrolyte  $\text{AgIO}_3$  (molecular mass = 283) the equilibrium which sets in is



If the solubility product constant  $K_{\text{sp}}$  of  $\text{AgIO}_3$  at a given temperature is  $1.0 \times 10^{-8}$ , what is the mass of  $\text{AgIO}_3$  contained in 100 ml of its saturated solution?

- a.  $2.83 \times 10^{-3}$  g
- b.  $1.0 \times 10^{-7}$  g
- c.  $1.0 \times 10^{-4}$  g
- d.  $28.3 \times 10^{-2}$  g

66. The first and second dissociation constants of an acid  $\text{H}_2\text{A}$  are  $1.0 \times 10^{-5}$  and  $5.0 \times 10^{-10}$  respectively. The overall dissociation constant of the acid will be

- a.  $5.0 \times 10^{15}$
- b.  $5.0 \times 10^{-15}$
- c.  $0.2 \times 10^5$
- d.  $5.0 \times 10^{-5}$

67. The pKa of a weak acid (HA) is 4.5. The pH of an aqueous buffered solution of HA in which 50 % of the acid is ionized is

- a. 2.5
- b. 9.5
- c. 7.0
- d. 4.5

68. Degree of hydrolysis of a salt of weak acid and a strong base is given by

- a.  $x = \sqrt{C / K_b}$
- b.  $x = \sqrt{(K_h / C)}$
- c.  $x = (K_h K_b / C)$
- d.  $x = \sqrt{(K_b / C)}$

69. 100 cc of HCl of pH value 1 is mixed with 100 cc of distilled water. The pH of the resultant solution is

- a. 1.3
- b. 1.7
- c. 2.3
- d. 1.9

70. The pKa of a weak acid, HA is 4.80. The  $\text{pK}_b$  of a weak base, BOH is 4.78. The pH of an aqueous solution of the corresponding salt, BA will be

- a. 9.58
- b. 4.79
- c. 7.01
- d. 9.22

## Brainteasers Objective Type Questions (Single choice only)

71. A certain buffer solution contains equal concentration of  $X^-$  and  $\text{HX}$ . The  $K_p$  for  $X^-$  is  $10^{-10}$ . The pH of the buffer is

- a. 6
- b. 10
- c. 4
- d. 14

72. What is the decreasing order of strength of the bases?

$\text{OH}^-$ ,  $\text{NH}_2^-$ ,  $\text{H} - \text{C} \equiv \text{C}^-$  and  $\text{CH}_3 - \text{CH}_2^-$  ?

- a.  $\text{CH}_3 - \text{CH}_2^- > \text{NH}_2^- > \text{H} - \text{C} \equiv \text{C}^- > \text{OH}^-$
- b.  $\text{H} - \text{C} \equiv \text{C}^- > \text{CH}_3 - \text{CH}_2^- > \text{NH}_2^- > \text{OH}^-$
- c.  $\text{OH}^- > \text{NH}_2^- > \text{H} - \text{C} \equiv \text{C}^- > \text{CH}_3 - \text{CH}_2^-$
- d.  $\text{NH}_2^- > \text{H} - \text{C} \equiv \text{C}^- > \text{OH}^- > \text{CH}_3 - \text{CH}_2^-$

73. The dissociation constants of acids HA and HB are  $3.2 \times 10^{-4}$  and  $2 \times 10^{-5}$  respectively. The ratio of the strengths HA to HB will be

- a. 4:1
- b. 1:4
- c. 16:1
- d. 1:16

74. Which of the following solutions will have pH close to 1.0?

- a. 100 ml of (M/10) HCl + 100 ml of (M/10) NaOH
- b. 55 ml of (M/10) HCl + 45 ml of (M/10) NaOH
- c. 10 ml of (M/10) HCl + 90 ml of (M/10) NaOH
- d. 75 ml of (M/10) HCl + 25 ml of (M/5) NaOH

75. A base dissolved in water, yields a solution with a hydroxyl ion concentration of  $0.05 \text{ mol L}^{-1}$ . The solution is

- a. acid
- b. neutral
- c. basic
- d. either (a) and (b)

76. The pH of the solution, produced when an aqueous solution of pH 5 is mixed with an equal volume of an aqueous solution of pH 3, is

- a. 3.3
- b. 4.3
- c. 2.5
- d. 6.3

77. 75 ml of 0.2 M HCl is mixed with 25 ml of 1 M HCl. To this solution, 300 ml of distilled water is added. What is the pH of the resultant solution?

- a. 1
- b. 2
- c. 4
- d. 0.2

78. The pH of a buffer solution, containing 0.2 mole

per litre of  $\text{CH}_3\text{COONa}$  and  $1.5 \text{ mol L}^{-1}$  of  $\text{CH}_3\text{COOH}$  is (Ka for acetic acid is  $1.8 \times 10^{-5}$ )

- a. 3.45
- b. 4.87
- c. 5.48
- d. 9.23

79. At 295 K, solubility of  $\text{AgCl}$  is  $1.435 \times 10^{-3} \text{ g L}^{-1}$ . Its solubility product is (take molecular weight of  $\text{AgCl} = 143.32$ )

- a.  $10^{-12}$
- b.  $10^{-10}$
- c.  $10^{-6}$
- d.  $10^{-16}$

80. The solubility product of  $\text{AgI}$  at  $25^\circ\text{C}$  is  $1.0 \times 10^{-16}$ . The solubility of  $\text{AgI}$  in  $10^{-4} \text{ N}$  solution of  $\text{KI}$  at  $25^\circ\text{C}$  is approximately.

- a.  $1.0 \times 10^{-6}$
- b.  $1.0 \times 10^{-8}$
- c.  $1.0 \times 10^{-12}$
- d.  $1.0 \times 10^{-16}$

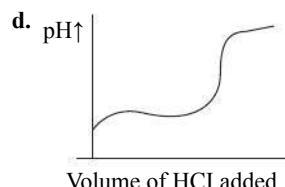
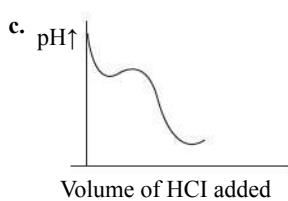
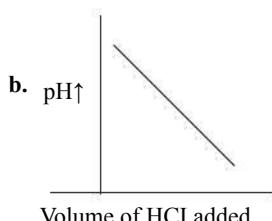
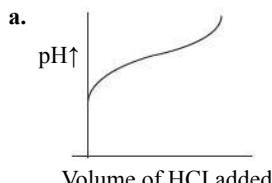
81. 100 ml of  $0.015 \text{ M}$  HCl solution is mixed with 100 ml of  $0.005 \text{ M}$  HCl. What is the pH of the resultant solution?

- a. 2.5
- b. 1.5
- c. 2
- d. 1

82. What is the pH of  $0.01 \text{ M}$  glycine solution? For glycine  $\text{Ka}_1 = 4.5 \times 10^{-3}$  and  $\text{Ka}_2 = 1.7 \times 10^{-10}$  at  $298 \text{ K}$

- a. 6.94
- b. 7.06
- c. 5.06
- d. 8.02

83. When 100 ml of  $0.1 \text{ M}$  NaCN solution is titrated with  $0.1 \text{ M}$  HCl solution the variation of pH of solution with volume of HCl added will be



84. 50 ml of  $0.1 \text{ M}$  HCl and 50 ml of  $0.2 \text{ M}$  NaOH are mixed. The pH of the resulting solution is

- a. 12.7
- b. 10.17
- c. 11.7
- d. 1.30

85.  $0.365 \text{ g}$  of HCl gas was passed through  $100 \text{ cm}^3$  of  $0.2 \text{ M}$  NaOH solution. The pH of the resulting solution would be

- a. 1
- b. 8
- c. 7
- d. 13
- e. 9

86. The  $\text{Ka}$  value of formic acid and acetic acid are respectively  $1.77 \times 10^{-4}$  and  $1.75 \times 10^{-5}$ . the ratio of the acid strength of  $0.1 \text{ N}$  acids is

- a. 0.1
- b. 0.3
- c. 3.178
- d. 100

87. On adding  $0.1 \text{ M}$  solution each of  $\text{Ag}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$  ions in a  $\text{Na}_2\text{SO}_4$  solution, species first precipitated is ( $\text{Ksp BaSO}_4 = 10^{-11}$ ,  $\text{Ksp CaSO}_4 = 10^{-6}$ ,  $\text{Ksp Ag}_2\text{SO}_4 = 10^{-5}$ )

- a.  $\text{CaSO}_4$
- b.  $\text{Ag}_2\text{SO}_4$
- c.  $\text{BaSO}_4$
- d. All of these

88. The  $\text{Ksp}$  of  $\text{Mg}(\text{OH})_2$  is  $1 \times 10^{-12}$ .  $0.01 \text{ M}$   $\text{Mg}^{2+}$  will precipitate at the limiting pH of

- a. 3
- b. 5
- c. 8
- d. 9

89. 20 ml of  $0.5 \text{ N}$  HCl and 35 ml of  $0.1 \text{ N}$  NaOH are mixed. The resulting solution will

- a. Turn methyl orange red
- b. Turn phenolphthalein solution pink
- c. Be neutral
- d. Be basic

90. 1 litre of  $0.5 \text{ M}$  KCl solution is electrolysed for one minute in a current of  $16.08 \text{ mA}$ . Considering 100 % efficiency, the pH of resulting solution will be

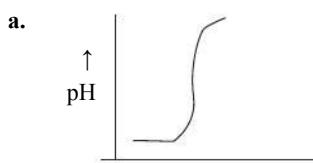
- a. 7
- b. 9
- c. 8
- d. 10

91. The hydrogen ion concentration of a  $10^{-8} \text{ M}$  HCl aqueous solution at  $298 \text{ K}$  ( $\text{Kw} = 10^{-14}$ ) is

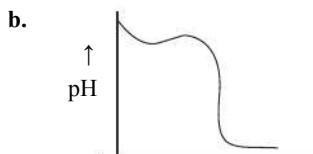
- a.  $9.525 \times 10^{-8} \text{ M}$
- b.  $1.0 \times 10^{-8} \text{ M}$
- c.  $1.0 \times 10^{-6} \text{ M}$
- d.  $1.0525 \times 10^{-7} \text{ M}$

## 5.86 ■ Ionic Equilibrium

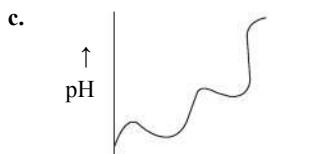
92. 40 ml of 0.1 M ammonia solution is mixed with 20 ml of 0.1 M HCl. What is the pH of the mixture? (pK<sub>b</sub> of ammonia solution is 4.74)
- 5.74
  - 9.26
  - 4.56
  - 7.06
93. HA is a weak acid. The pH of 0.1 M HA solution is 2. What is the degree of dissociation ( $\alpha$ ) of HA?
- 0.1
  - 0.2
  - 0.4
  - 0.51
94. At 25°C the value of pK<sub>b</sub> (K<sub>b</sub> being the dissociation constant as a base) for NH<sub>3</sub> in aqueous solution is 4.7. What is the pH of a 0.1 M aqueous solution of NH<sub>4</sub>Cl with 0.01 M NH<sub>3</sub> (approximately)?
- 9
  - 8.3
  - 9.6
  - 10
95. A weak acid, HA has a K<sub>a</sub> of  $1.00 \times 10^{-5}$ . If 0.100 mol of this acid is dissolved in one litre of water, the percentage of acid dissociated at equilibrium is closest to
- 99.0 %
  - 1.00 %
  - 99.9 %
  - 0.100 %
96. The aqueous solutions of HCOONa, C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub>Cl and KCN are respectively
- Basic, acidic, basic
  - Basic, neutral, neutral
  - Acidic, acidic, basic
  - Acidic, basic, neutral
  - Basic, neutral, basic
97. Which is the best choice for weak base-strong acid titration?
- Methyl acid
  - Phenolphthalein
  - Litmus
  - Phenol acid
98. Addition of sodium acetate to 0.1 M acetic acid will cause
- Increase of pH
  - No change in pH
  - Change in pH that cannot be predicted
  - Decrease in pH
99. Solubility product of Mg(OH)<sub>2</sub> at ordinary temp. is  $1.96 \times 10^{-11}$ . pH of a saturated soln. of Mg(OH)<sub>2</sub> will be—
- 10.53
  - 6.78
  - 3.56
  - 3.66
100. Which one is the correct graph for the corresponding acid base titration?



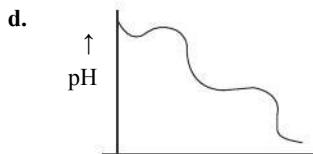
Volume of strong base added to a monobasic strong acid



Volume of strong base added to a monobasic weak acid



Volume of strong base added to a weak dibasic acid



Volume of strong base added to a weak diacidic base

101. The pH of a solution obtained by mixing 50 ml of 1 N HCl and 30 ml of 1 N NaOH is [ log 2.5 = 0.3979 ]
- 11.045
  - 0.6021
  - 2.768
  - 1.0009
  - 14.897
102. A buffer solution is prepared by mixing equal concentration of acid (ionization constant K<sub>a</sub>) and a salt. The pH of buffer is
- $14 - pK_a$
  - $pK_a + 7$
  - $pK_a$
  - $pK_a + 1$
103. Equimolar solutions of the following were prepared in water separately. Which one of the solutions will record the highest pH?
- MgCl<sub>2</sub>
  - CaCl<sub>2</sub>
  - SrCl<sub>2</sub>
  - BaCl<sub>2</sub>

104. The values of  $K_p_1$  and  $K_p_2$  for the reactions



are in ratio of 9:1. If degree of dissociation of X and A be equal, then total pressure at equilibrium (1) and (2) are in the ratio:

- a. 36:1      b. 1:1  
c. 3:1      d. 1:9

105. For a concentrated solution of a weak electrolyte  $A_x B_y$  of concentrated 'C', the degree of dissociation  $\alpha$  is given as

- a.  $\alpha = (K_{eq} / C^{xy})$   
b.  $\alpha = (K_{eq} / C^{xy})$   
c.  $\alpha = K_{eq} / C^{x+y-1} x^x y^y)^{1/(x+y)}$   
d.  $\alpha = K_{eq} C / (xy)$   
e.  $\alpha = K_{eq} / C(x+y)$

106. The solubility of  $BaSO_4$  in water is

$2.33 \times 10^{-3}$  g-L<sup>-1</sup>. Its solubility product will be (molecular weight of  $BaSO_4$  = 233)

- a.  $1 \times 10^{-10}$       b.  $1 \times 10^{-15}$   
c.  $1 \times 10^{-5}$       d.  $1 \times 10^{-20}$

107. If  $K_{sp}$  of  $PbBr_2$  is  $8 \times 10^{-5}$  and it is 80% dissociated in solution find its solubility?

- a. 0.027 m/L      b. 0.038 m/L  
c. 0.017 m/L      d. 0.034 m/L

108. Ascorbic acid,  $H_2C_6H_6O_6$ , is a polyprotic acid containing two ionizable hydrogens.  $K_{a1}$  is  $8.0 \times 10^{-5}$  and  $K_{a2}$  is  $1.6 \times 10^{-12}$ . Calculate the pH of a  $2.0 \times 10^{-3}$  M solution of ascorbic acid.

- a. 3.40      b. 0.340  
c. 2.70      d. 0.270

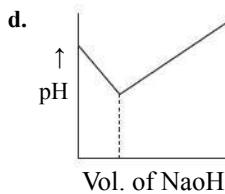
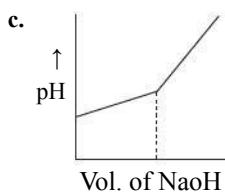
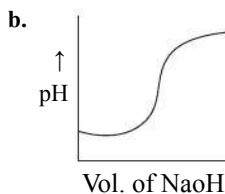
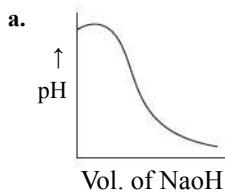
109. The solubility products of  $CuS$ ,  $Ag_2S$  and  $HgS$  are respectively  $10^{-37}$ ,  $10^{-49}$  and  $10^{-54}$ . The solubilities (in mol.lit<sup>-1</sup>) of these sulphides are in the descending order,

- a.  $CuS > Ag_2S > HgS$   
b.  $Ag_2S > HgS > CuS$   
c.  $HgS > Ag_2S > CuS$   
d.  $Ag_2S > CuS > HgS$

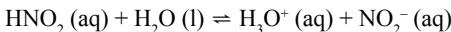
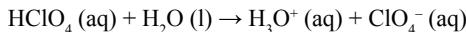
110. Equal volumes of three acid solutions of pH 3, 4, and 5 are mixed in a vessel. What will be the  $H^+$  ion concentration in the mixture?

- a.  $3.7 \times 10^{-3}$  M      b.  $1.11 \times 10^{-3}$  M  
c.  $1.11 \times 10^{-4}$  M      d.  $3.7 \times 10^{-4}$  M

111. Which one of these curves represents the graph of pH during the titration of NaOH and HCl (aq) here



112. From the following chemical reactions determine the relative Bronsted–Lowry acid strengths (Strongest to weakest).



- a.  $HClO_4 > HNO_2 > H_3O^+$   
b.  $HClO_4 > H_3O^+ > HNO_2$   
c.  $H_3O^+ > HNO_2 > HClO_4$   
d.  $H_3O^+ > HClO_4 > HNO_2$

113. Four species are listed below:

- (I)  $HCO_3^-$       (II)  $H_3O^+$   
(III)  $HSO_4^-$       (IV)  $HSO_3F$

Which one of the following is the correct sequence of their acid strength?

- a. IV < II < III < I  
b. II < III < I < IV

- c. I < III < II < IV  
d. III < I < IV < II
- 114.** What is the pH of a solution prepared by mixing 100 ml of 0.020 M  $\text{Ca}(\text{OH})_2$  with 50.00 ml of 0.100M NaOH? Assume that the volumes are additive.  
 a. 10.87      b. 11.78  
 c. 12.00      d. 12.78
- 115.** Para-Aminobenzoic acid (PABA),  $\text{H}_2\text{NC}_6\text{H}_4(\text{COOH})$ , is used in some sunscreens and hair conditioning products. Calculate the pH of an aqueous solution with  $[\text{PABA}] = 0.030 \text{ M}$  and  $K_a = 2.2 \times 10^{-5}$ .  
 a. 2.09      b. 4.98  
 c. 6.18      d. 3.09
- 116.** Three sparingly soluble salts  $\text{A}_2\text{X}$ ,  $\text{AX}$  and  $\text{AX}_3$  have the same solubility product. Their solubilities will be in the order  
 a.  $\text{AX}_3 > \text{AX} > \text{A}_2\text{X}$   
 b.  $\text{AX}_3 > \text{A}_2\text{X} > \text{AX}$   
 c.  $\text{AX} > \text{AX}_3 > \text{A}_2\text{X}$   
 d.  $\text{AX} > \text{A}_2\text{X} > \text{AX}_3$
- 117.** At  $25^\circ\text{C}$ , the pH of a vinegar solution is 2.60. What are the values of  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  in the solution?  
 a.  $2.51 \times 10^{-3} \text{ M}$ ,  $3.99 \times 10^{-12} \text{ M}$   
 b.  $2.30 \text{ M}$ ,  $12.40 \text{ M}$   
 c.  $3.51 \times 10^{-4} \text{ M}$ ,  $3.99 \times 10^{-10} \text{ M}$   
 d.  $2.51 \times 10^{-3} \text{ M}$ ,  $1.28 \times 10^{-4} \text{ M}$
- 118.** Which of the following are weak diprotic acids?  
 a. Hydrocyanic acid – HCN, sulphuric acid –  $\text{H}_2\text{SO}_4$ , phosphoric acid –  $\text{H}_3\text{PO}_4$   
 b. Carbonic acid –  $\text{H}_2\text{CO}_3$ , oxalic acid –  $\text{H}_2\text{C}_2\text{O}_4$ , sulphurous acid –  $\text{H}_2\text{SO}_3$   
 c. Formic acid –  $\text{HCOOH}$ , acetic acid –  $\text{CH}_3\text{COOH}$ , benzoic acid –  $\text{C}_6\text{H}_5\text{COOH}$   
 d. Carbonic acid –  $\text{H}_2\text{CO}_3$ , hydrosulphuric acid –  $\text{H}_2\text{S}$ , acetic acid –  $\text{CH}_3\text{COOH}$
- 119.** Which of the following salts are acidic?  
 a.  $\text{NH}_4\text{Cl}$ ,  $\text{CuCl}_2$ ,  $\text{AlCl}_3$   
 b.  $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$   
 c.  $\text{NaCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{Na}_2\text{CO}_3$   
 d.  $\text{NaCH}_3\text{CO}_2$ ,  $\text{KCH}_3\text{CO}_2$ ,  $\text{RbCH}_3\text{CO}_2$
- 120.** An acidic solution at  $25^\circ\text{C}$  will have a hydronium ion concentration \_\_\_\_\_ and a pH value of \_\_\_\_\_.  
 a.  $[\text{H}_3\text{O}^+] < 1 \times 10^{-7} \text{ M}$ ,  $\text{pH} < 7.00$   
 b.  $[\text{H}_3\text{O}^+] < 1 \times 10^{-7} \text{ M}$ ,  $\text{pH} > 7.00$   
 c.  $[\text{H}_3\text{O}^+] > 1 \times 10^{-7} \text{ M}$ ,  $\text{pH} < 7.00$   
 d.  $[\text{H}_3\text{O}^+] > 1 \times 10^{-7} \text{ M}$ ,  $\text{pH} > 7.00$
- 121.** The decreasing order of acidic nature of  $\text{H}_2\text{SO}_4$  (I),  $\text{H}_3\text{PO}_4$  (II), and  $\text{HClO}_4$  (III) is  
 a. I > II > III      b. I > III > II  
 c. III > I > II      d. III > II > I
- 122.** Arrange the following 0.5 M aqueous solutions in order of increasing pH  
 NaOH, HBr,  $\text{NaCH}_3\text{CO}_2$ , KBr,  $\text{NH}_4\text{Br}$   
 a. HBr,  $\text{NH}_4\text{Br}$ , KBr,  $\text{NaCH}_3\text{CO}_2$ , NaOH  
 b. NaOH,  $\text{NaCH}_3\text{CO}_2$ , KBr,  $\text{NH}_4\text{Br}$ , HBr  
 c. NaOH,  $\text{NaCH}_3\text{CO}_2$ ,  $\text{NH}_4\text{Br}$ , KBr, HBr  
 d. HBr, KBr,  $\text{NH}_4\text{Br}$ ,  $\text{NaCH}_3\text{CO}_2$ , NaOH
- 123.** The pH values of 2 M solutions of  $\text{CH}_3\text{COOH}$  (I),  $\text{CH}_3\text{COOK}$  (II),  $\text{CH}_3\text{COONH}_4$  (III), and KOH (IV) will be in the order  
 a. IV > III > II > I      b. IV > II > III > I  
 c. I > III > II > IV      d. II > I > III > IV
- 124.**  $\text{P}_3\text{Q}_2$  is a sparingly soluble salt of molar mass M ( $\text{g}\cdot\text{mol}^{-1}$ ) and solubility  $\times \text{g}\cdot\text{lit}^{-1}$ . The ratio of the molar concentration of  $\text{Q}^{3-}$  to the solubility product of the salt is  
 a.  $\frac{1}{54} \frac{\text{M}^4}{\text{x}^4}$       b.  $\frac{\text{M}^3}{27 \text{x}^3}$ .  
 c.  $\frac{\text{M}^3}{27^{1/2} \text{x}^{3/2}}$       d.  $54 \frac{\text{x}^5}{\text{M}^5}$ .
- 125.** An acidic solution at  $25^\circ\text{C}$  has  
 a.  $[\text{H}_3\text{O}^+] = [\text{OH}^-] > 1 \times 10^{-7} \text{ M}$   
 b.  $[\text{H}_3\text{O}^+] < 1 \times 10^{-7} \text{ M} > [\text{OH}^-]$   
 c.  $[\text{H}_3\text{O}^+] > [\text{OH}^-] > 1 \times 10^{-7} \text{ M}$   
 d.  $[\text{H}_3\text{O}^+] > 1 \times 10^{-7} \text{ M} > [\text{OH}^-]$
- 126.** Consider the following:  
 (I)  $\text{KCl}$       (II)  $\text{NH}_4\text{Cl}$   
 (III)  $\text{KCN}$       (IV)  $\text{HCl}$
- The correct sequence in the order of increasing pH of 0.2 M solution of these compounds will be  
 a. III < II < I < IV  
 b. IV < II < I < III  
 c. IV < III < II < I  
 d. IV < I < II < III

127. 0.15 mole of pyridinium chloride has been added to  $500 \text{ cm}^3$  of 0.2 M pyridine solution. What is the pH of the resulting solution assuming no change in volume? ( $K_b$  for pyridine =  $1.5 \times 10^{-9}$  M)

- a. 5
- b. 6
- c. 7
- d. 8

128. What quantity of sodium acetate must be added to 1.00 litre of a 0.200 ?M acetic acid

( $K_a = 1.8 \times 10^{-5}$ ) solution to form a buffer of pH = 4.30?

- a.  $7.18 \times 10^{-2}$  moles
- b.  $3.62 \times 10^{-5}$  moles
- c.  $7.18 \times 10^{-3}$  moles
- d.  $4.15 \times 10^{-9}$  moles

129.  $K_{sp} = 1.39 \times 10^{-8}$  at 25 °C for  $\text{PbI}_2$ . What is the concentration of lead ion ( $\text{Pb}^{2+}$ ) in a solution containing 0.15 ?M NaI?

- a.  $3.25 \times 10^{-2}$  M
- b.  $1.18 \times 10^{-4}$  M
- c.  $6.18 \times 10^{-7}$  M
- d.  $9.27 \times 10^{-8}$  M

130. In a 50mL of 0.1 M HCl solution, 10 mL of 0.1 M NaOH is added and the resulting solution is diluted to 100mL. Wha is change in pH of the HCl solution ?

- a. 4.04
- b. 0.4
- c. 0.1
- d. 0.2

### Multiple Correct Answer Type Questions

131. For a series of weak bases of the same concentration, which statement is/are incorrect?

- a. The rate of production of hydroxide ion increases with  $\text{pK}_b$ .
- b. The larger the value of  $\text{pK}_b$  the more exothermic is the reaction of the base with water.
- c. The pOH of water is larger in all cases.
- d. The larger the value of  $\text{pK}_b$  the smaller the value of pH.

132.  $\text{Mg(OH)}_2$  is a slightly soluble salt with a  $K_{sp}$  of  $1.8 \times 10^{-11}$ . If a solution is 0.15 M in  $\text{Mg}(\text{NO}_3)_2$  and 0.15 M in  $\text{NH}_3$  ( $K_b = 1.8 \times 10^{-5}$ ), which statement is/ are incorrect?

- a.  $\text{Mg(OH)}_2$  will not precipitate because of the presence of the weak acid  $\text{NH}_4^+$ .
- b. Addition of HCl to the solution decreases the solubility of  $\text{Mg(OH)}_2$ .
- c. The concentration of  $\text{OH}^-$  will bwe larger than of  $\text{NH}_4^+$

133. Equimolar solution of AOH and BOH are prepared. The I.P. of A and B are 5.1 and 13.0 eV respectively. The EN of A and B are 0.9 and 3.2 respectively. From the data, pick out the correct statements

- a. BOH solution will have a pH > 7
- b. solution of BOH will give effervescence with sodium carbonate
- c. treatment of  $\text{NH}_4\text{Cl}$  with AOH will lead to evolution of  $\text{NH}_3$ .
- d. phenolphthalein will give pink colour with AOH solution.

134. A solution contains 0.01 M each of NaCl and  $\text{Na}_2\text{CrO}_4$  solid  $\text{AgNO}_3$  is gradually added to it. Which is/ are not true?

[Given  $\text{K}_{sp}(\text{AgCl}) = 1.7 \times 10^{-10} \text{ M}^2$ ;  $\text{K}_{sp}(\text{Ag}_2\text{Cr}_2\text{O}_4) = 1.9 \times 10^{-12} \text{ M}^3$ ]

- a.  $\text{CrO}_4^{2-}$  ions are precipitated first
- b.  $\text{Cl}^-$  ions are precipitated first
- c. the second ion states precipitating when half of the first ion is precipitate
- d. both  $\text{Cl}^-$  and  $\text{CrO}_4^{2-}$  ions are precipitated together

135. Which one of the following statement is/are true?

- a.  $\text{pH} + \text{pOH} = 14$  for all aqueous solutions
- b. pH of  $1 \times 10^{-8}$  M HCl is 8
- c. conjugate base of  $\text{H}_2\text{PO}_4^-$  is  $\text{HPO}_4^{2-}$
- d. 96,500 coulombs of electricity when passed through a  $\text{CuSO}_4$  solution deposits 1 gram equivalent of copper at the cathode.

136. Equal volumes of the following  $\text{Ca}^{2+}$  and  $\text{F}^-$  solutions are mixed. In which of the solutions will precipitation occurs?

[ $\text{K}_{sp}$  of  $\text{CaF}_2 = 1.7 \times 10^{-10}$ ]

- a.  $10^{-2}$  M  $\text{Ca}^{2+} + 10^{-5}$  M  $\text{F}^-$
- b.  $10^{-3}$  M  $\text{Ca}^{2+} + 10^{-3}$  M  $\text{F}^-$
- c.  $10^{-4}$  M  $\text{Ca}^{2+} + 10^{-2}$  M  $\text{F}^-$
- d.  $10^{-2}$  M  $\text{Ca}^{2+} + 10^{-3}$  M  $\text{F}^-$

137. An acid base indicator ( $\text{Ka} = 10^{-5}$ ) has its pH range 4.4 – 6. The correct statement amongst the following is/are

- a. the indicator will be suitable for the titration of a strong acid against a weak base
- b. the acidic colour of the indicator will predominate if the concentration of acidic form is 6 times more than that of the basic form.

## 5.90 ■ Ionic Equilibrium

- c. the indicator will be suitable for the titration of a weak acid against a strong base
- d. the basic colour of the indicator will prevail when concentration of basic form will be at least 10 times more than that of the acidic form.
138. If S and  $K_{sp}$  be the solubility and solubility product respectively, then
- for  $\text{AgCl}$ :  $S = \sqrt{K_{sp}}$  and for  $\text{Al}(\text{OH})_3$ :  $S = \sqrt[3]{(K_{sp}/9)}$
  - for  $\text{CaSO}_4$ :  $S = \sqrt{K_{sp}}$  and for  $\text{KI}_3$ :  $S = \sqrt[5]{K_{sp}}$
  - for  $\text{Ca}_3(\text{PO}_4)_2$ :  $S = \sqrt[5]{(K_{sp}/108)}$  and for  $\text{AgI}$ :  $S = \sqrt{K_{sp}}$
  - for  $\text{Bi}_2\text{S}_3$  and for  $\text{Ca}_3(\text{PO}_4)_2$  both :  $S = \sqrt[5]{(K_{sp}/108)}$
139. Which of the following statement is/are incorrect?
- Solubility of  $\text{AgCl}$  is less in 0.5 M  $\text{KCl}$  solution than pure water
  - Solubility of  $\text{AgCl}$  is more in 0.5 M  $\text{CaCl}_2$  than water
  - Solubility of  $\text{AgCl}$  is more in 1 M  $\text{AgNO}_3$  than pure water
  - Solubility of  $\text{AgCl}$  is more in  $\text{NH}_3$  than  $\text{H}_2\text{O}$
140. Complex formation in a solution results in
- change in solubility of sparingly soluble salt
  - change in pH of solution
  - not change in freezing point
  - change in chemical nature
141.  $\text{A(OH)}_2$  is a partially soluble substance and its  $K_{sp}$  value is  $4 \times 10^{-12}$ , which of the following statement is/are correct?
- the solubility is unaffected by pH of the medium
  - its solubility has been decreased in a buffered medium at pH at 1 L
  - its solubility has been increased in a buffered medium having pH at 9
  - its saturated solution has pH is equal to 10.3
142. The acid ionization (hydrolysis) constant of  $\text{Zn}^{2+}$  is  $1.0 \times 10^{-9}$ . Which of the following statement are incorrect.
- the  $[\text{H}_3\text{O}^+]$  ion concentration in 0.001 M  $\text{ZnCl}_2$  solution is  $1.0 \times 10^{-4}$ .
  - the pH of 0.001 M  $\text{ZnCl}_2$  solution is 6.
- c. the basic dissociation constant of  $\text{Zn}(\text{OH})^+$  is  $1.0 \times 10^{-5}$ .
- d. the basic dissociation constant of  $\text{Zn}(\text{OH})^+$  is  $1.0 \times 10^5$ .
143. Which of the following solution(s) have pH between 6 and 7?
- $2 \times 10^{-6}$  M  $\text{KOH}$
  - $2 \times 10^{-6}$  M  $\text{HCl}$
  - $10^{-8}$  M  $\text{HCl}$
  - $10^{-12}$  M  $\text{KOH}$
144. Which of the following solutions will have no effect on pH on dilution?
- 0.3 M  $\text{CH}_3\text{COOK}$
  - 2.4 M  $\text{CH}_3\text{COONH}_4$
  - 0.2 M  $\text{NH}_4\text{OH} + 0.2$  M  $\text{NH}_4\text{Cl}$
  - 0.3 M  $\text{H}_2\text{CO}_3 + 0.3$  M  $\text{NaHCO}_3$
145. During the titration of a mixture of  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$  and inert substances against  $\text{HCl}$
- phenolphthalein can be used to detect the end point when half equivalent of  $\text{Na}_2\text{CO}_3$  and full equivalent  $\text{NaOH}$  is consumed
  - phenolphthalein can be used to detect the second end point
  - methyl orange can be used to detect the final end point
  - methyl orange can be used to detect the first end point
146. Which of the following solution will have pH close to 7?
- 10 ml of M/10  $\text{HCl} + 100$  ml of M/10  $\text{Mg}(\text{OH})_2$
  - 100 ml of M/10  $\text{H}_2\text{SO}_4 + 50$  ml of M/10  $\text{NaOH}$
  - 200 ml of M/10  $\text{KCl} + 200$  ml of M/10  $\text{NaOH}$
  - 2 M solution of  $\text{CH}_3\text{COONH}_4$  ( $K_a = K_b$ )
147. 100 ml solution having 0.2 M HA (weak acid,  $K_a = 1.0 \times 10^{-5}$ ) and 0.2 N  $\text{NaA}$ , 200 ml of 0.1 M  $\text{NaOH}$  has been added. Furthermore, diluted to 1L. Which of the following statement is correct?
- initially, the solution have pH equal to 3.
  - in the final solution, the concentration of  $[\text{OH}^-]$  is  $10^{-9}$  M.
  - after the addition of  $\text{NaOH}$ , the pH of solution increase by four unit
  - after the addition of base, the solution losses buffering action and restores after the addition of acid
148. Which statement is/are not true about buffers?
- Buffers consists of a strong acid and its conjugate base

- b.** Buffers have a pH of 7.
- c.** Buffers resist change in pH upon addition of small amounts of strong acid or strong base.
- d.** A buffer does not change pH on addition of a strong acid or strong base.
- 149.** Solubility ( $S$ ) of calcium phosphate (molecular mass,  $M$ ) is ' $x$ ' g per 100 ml at 300 K, its solubility product at 300 K will be approximately
- $10^7 (x / M)^5$
  - $10^6 (x / M)^5$
  - $10^8 (x / M)^5$
  - $108 S^5$
- 150.** Acetic acid and aq.  $\text{NH}_3$  are weak monobasic acid and weak monoacidic base respectively and  $K_a$  of acetic acid is equal to  $K_b$  of aq.  $\text{NH}_3$ . Which of the following statements are correct?
- all the above mixing would result in neutral solution having pH = 7 at 25°C
  - if aq.  $\text{NH}_3$  is exactly half neutralized by HCl, then pOH of resulting solution is equal to  $pK_b$ .
  - if acetic acid is exactly half neutralized by NaOH, then pH of resulting solution is equal to  $pK_a$ .
  - if acetic acid is exactly neutralized by aq.  $\text{NH}_3$ , then pH of resulting solution is equal to  $\frac{1}{2} pK_w$ .
- 151.** Equal volumes of following solutions are mixed, in which case the pH of resulting solution will be average value of pH of two solutions?
- pH = 3 ( $\text{HNO}_3$ ) and pH = 5 ( $\text{HNO}_3$ )
  - pH = 2 ( $\text{HNO}_3$ ) and pH = 12 (KOH)
  - pH = 4.5 ( $\text{CH}_3\text{COOH}$ ) and pH = 9.5 ( $\text{NH}_3$ ) (aq) ( $K_a \text{CH}_3\text{COOH} = K_b \text{NH}_4\text{OH}$ )
  - pH = 3 (HCN) and pH = 11 (NaOH) ( $K_a$  of HCN =  $10^{-10}$ )
- 152.** Which one of the following statement is/are incorrect?
- Bronsted-Lowry theory could not explain the acidic nature of  $\text{BCl}_3$
  - the pH of 0.01 M NaOH solution is 2.
  - the ionic product of water at 25°C is  $10^{-10}$  mol<sup>2</sup> lit<sup>-2</sup>.
  - the pH of a solution can be calculated using the equation  $\text{pH} = \log [\text{H}^+]$
- 153.** What is/are correct expression for the weak acid HA?
- $\text{pKa} = 14 - \text{pK}_b$
  - $\text{pKa} = \log_{10} K_a$
  - $\text{pKa} = \text{pH} - \log_{10} \{[\text{A}^-] / [\text{HA}]\}$
  - $K_a = [\text{H}_3\text{O}^+] [\text{A}^-] / [\text{Ha}]$
- 154.** Which of the following statements about pH and  $\text{H}^+$  ion concentration is/are correct?
- addition of one drop of concentrated HCl in  $\text{NH}_4\text{OH}$  solution decreases pH of the solution.
  - a solution of the mixture of one equivalent of each of  $\text{CH}_3\text{COOH}$  and NaOH has a pH of 7.
  - pH of pure neutral water is not zero.
  - a cold and concentrated  $\text{H}_2\text{SO}_4$  has lower  $\text{H}^+$  ion concentration than a dilute solution of  $\text{H}_2\text{SO}_4$ .
- 155.** Which one of the following is/are buffer solution?
- 0.8 M  $\text{H}_2\text{S} + 0.8 \text{ M KHS}$
  - $2\text{M C}_6\text{H}_5\text{NH}_2 + 2\text{M C}_6\text{H}_5\text{NH}_3^+$
  - 3M  $\text{H}_2\text{CO}_3 + 3\text{M KHCO}_3$
  - 0.05 M  $\text{KClO}_4 + 0.05 \text{ M HClO}_4$
- 156.** In the reaction:
- $$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{H}_2\text{O} \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+} + \text{H}_3\text{O}^+$$
- $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is an acid
  - $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is a base
  - $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$  is a conjugate acid
  - $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$  is a conjugate base
- 157.** Which of the following solution will have pH = 13 on assuming complete dissociation
- 100 ml of solution of 0.1 N  $\text{Mg}(\text{OH})_2$
  - 0.56 g of KOH in 100 ml solution
  - 4 g of NaOH in 500 ml solution.
  - 100 ml of solution of 0.05 M  $\text{Mg}(\text{OH})_2$
- 158.** Factor influencing the degree of dissociation of a weak electrolyte is
- Dilution
  - Temperature

- c. Presence of common ions  
d. Nature of solvent

159. Acid strength can be directly proportional to  
a. Ka                    b. pH  
c. pOH                d.  $H^+$

160. Which of the following mixtures can act as buffer?  
a.  $H_2CO_3 + KOH$  (2 : 5 : 1 molar ratio)  
b.  $H_2CO_3 + KOH$  (2 : 5 : 3 molar ratio)  
c.  $NH_4OH + HNO_3$  (6 : 4 molar ratio)  
d.  $NH_4OH + HNO_3$  (3 : 5 molar ratio)

c.  $BH_3, BF_3, Cu^{2+}, CO_2$   
d.  $Cl^-, OH^-, NH_3, H_2O$

164. From the following chemical reactions determine the relative Bronsted-Lowry base strengths (strongest to weakest).

$$HNO_3 \text{ (aq)} + H_2O \text{ (l)} \rightarrow H_3O^+ \text{ (aq)} + NO_3^- \text{ (aq)}$$
$$HF \text{ (aq)} + H_2O \text{ (l)} \rightleftharpoons H_3O^+ \text{ (aq)} + F^- \text{ (aq)}$$

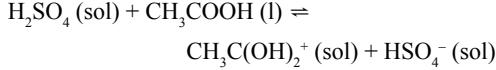
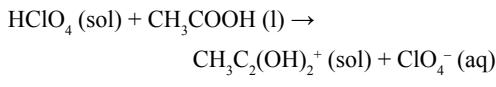
a.  $F^- > H_2O > NO_3^-$   
b.  $F^- > NO_3^- > H_2O$   
c.  $HNO_3 > H_3O^+ > HF$

## **Linked-Comprehension Type Questions**

## Comprehension 1

According to Bronsted concept acid is proton donor while base is proton accepter. According to Lewis an acid is electron deficient and electron accepter while a base is electron efficient and electron donor. The acidic strength depends upon electro negativity difference, oxidation number etc.

- 161.** From the following chemical reactions determine the relative Bronsted–Lowry acid strengths (strongest to weakest).



- a.  $\text{HClO}_4 > \text{CH}_3\text{C}(\text{OH})_2^+ > \text{H}_2\text{SO}_4$
  - b.  $\text{HClO}_4 > \text{CH}_3\text{COOH} > \text{H}_2\text{SO}_4$
  - c.  $\text{HClO}_4 > \text{H}_2\text{SO}_4 > \text{CH}_3\text{C}(\text{OH})_2^+$
  - d.  $\text{HClO}_4 > \text{H}_2\text{SO}_4 > \text{CH}_3\text{COOH}$

162. For  $\text{Cu}^{2+}$  and  $\text{CO}_2$ , which will behave as a Lewis acid toward  $\text{OH}^-$  in water?

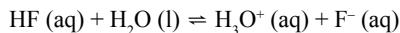
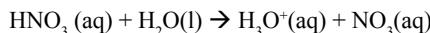
  - a. Only  $\text{CO}_2$
  - b. Only  $\text{Cu}^{2+}$
  - c. Neither  $\text{Cu}^{2+}$  nor  $\text{CO}_2$
  - d. Both  $\text{Cu}^{2+}$  and  $\text{CO}_2$

- 163.** Identify the set of Lewis acids:

  - $\text{CH}_3^-$ ,  $\text{NH}_2^-$ ,  $\text{OH}^-$ ,  $\text{F}^-$
  - $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$

- c.  $\text{BH}_3$ ,  $\text{BF}_3$ ,  $\text{Cu}^{2+}$ ,  $\text{CO}_2$   
d.  $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$

- 164.** From the following chemical reactions determine the relative Bronsted–Lowry base strengths (strongest to weakest).



- a.  $\text{F}^- > \text{H}_2\text{O} > \text{NO}_3^-$
  - b.  $\text{F}^- > \text{NO}_3^- > \text{H}_2\text{O}$
  - c.  $\text{HNO}_3 > \text{H}_3\text{O}^+ > \text{HF}$
  - d.  $\text{NO}_3^- > \text{H}_2\text{O} > \text{F}^-$

## Comprehension 2

pH scale was introduced by Sorenson to measure acidity or basicity of a solution. pH value of a solution does not instantaneously give us an idea of the relative strength of the solution. At higher concentration, in place of pH, Hammelt acidity functions are used. Buffer solution is the solution whose pH, on addition of a small amount of strong acid or a base, does not change much.

- 165.** The degree of dissociation of a weak monoprotic acid can be given as:

a.  $\alpha = \frac{1}{1 + 10^{(pK_a + pH)}}$

**b.**  $\alpha = \frac{1}{1 + 10^{(pK_a - pH)}}$

c.  $\alpha = \frac{1}{1 + 10^{(pH - pK_a)}}$

d.  $\alpha = \frac{1}{1 + 10^{(pK_a - pH)}}$

166. Given a solution of acetic acid. How many times of the acid concentration, acetate salt should be added to obtain a solution with pH = 7.0? [ $K_a$  for dissociation of  $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$ ]

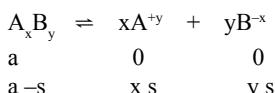
- a. 170 times
  - b. 137 times
  - c. 173 times
  - d. 172 times

- 167.** pH = 7.40 K<sub>1</sub> of H<sub>2</sub>CO<sub>3</sub> = 4.5 × 10<sup>-7</sup>. What will be the ratio of [HCO<sub>3</sub><sup>-</sup>] to [H<sub>2</sub>CO<sub>3</sub>]?



## Comprehension 3

For a general reaction given, below the value of solubility product can be given as:



$$K_{sp} = (x s)^x \cdot (y s)^y$$

or

$$K_{sp} = x^x y^y (s)^{x+y}$$

Solubility product gives us not only an idea about the solubility of an electrolyte in a solvent but also helps in explaining concept of precipitation and calculation of  $H^+$  ion,  $OH^-$  ion. It is also useful in qualitative analysis for the identification and separation of basic radicals

- 168.** Which metal sulphides can be precipitated from a solution that is 0.01 M in  $Mn^{2+}$ ,  $Zn^{2+}$ ,  $Pb^{2+}$  and  $Cu^{2+}$  and 0.10 M in  $H_2S$  at a pH of 1.0?

Metal sulphide	$K_{sp}$
MnS	$3 \times 10^{16}$
ZnS	$3 \times 10^{-2}$
PbS	$3 \times 10^{-7}$
CuS	$6 \times 10^{-16}$
a. CuS	b. MnS
c. ZnS, PbS, CuS	d. PbS, CuS

- 169.** Potassium chromate is slowly added to a solution containing 0.20 M  $AgNO_3$  and 0.20 M  $Ba(NO_3)_2$ . Describe what happens if the  $K_{sp}$  for  $Ag_2CrO_4$  is  $1.1 \times 10^{-12}$  and the  $K_{sp}$  of  $BaCrO_4$  is  $1.2 \times 10^{-10}$ .

- a. The  $Ag_2CrO_4$  precipitates first out of solution and then  $BaCrO_4$  precipitates.
- b. The  $BaCrO_4$  precipitates first out of solution.
- c. Both  $Ag_2CrO_4$  and  $BaCrO_4$  precipitate simultaneously out of solution.
- d. Neither  $Ag_2CrO_4$  nor  $BaCrO_4$  precipitates out of solution.

- 170.** What is the molar solubility of  $Cu(OH)_2$  in 1.0 M  $NH_3$  if the deep blue complex ion  $Cu(NH_3)_4^{2+}$  forms? The  $K_{sp}$  for  $Cu(OH)_2$  is  $1.6 \times 10^{-19}$  and the  $K_f$  for  $Cu(NH_3)_4^{2+}$  is  $1.1 \times 10^{13}$ .
- a.  $7.1 \times 10^{-4}$  M
  - b.  $7.6 \times 10^{-3}$  M
  - c.  $6.7 \times 10^{-3}$  M
  - d.  $5.6 \times 10^{-3}$  M

- 171.** The solubility product of  $AgI$  in water is  $4.9 \times 10^{-11}$  at a given temperature. The solubility of  $AgI$  in 0.001 M  $KI$  solution is
- a.  $7.0 \times 10^{-7}$
  - b.  $4.8 \times 10^{-3}$
  - c.  $7.0 \times 10^{-8}$
  - d.  $5.9 \times 10^{-10}$

## Comprehension 4

Salt hydrolysis is a phenomenon in which the cation or anion or both of a salt react with water to produce acidity or basicity. The extent of hydrolysis is measured in terms of degree of hydrolysis ( $h$ ). For various type of salts there are different relations to find  $K_h$  (Hydrolysis constant)  $h$ , and pH of the aqueous solution.

- 172.** The hydrolysis const for  $ZnBr_2$  can be given as

$$\begin{array}{ll} a. k_h = \frac{K_w}{K_b} & b. k_h = \frac{K_w}{K_b^2} \\ c. k_h = \frac{K_b}{K_w^2} & d. k_h = \frac{K_w^2}{K_b} \end{array}$$

- 173.** Which of the following salts on dissolving in water produce acidic solution

- (i)  $KCN$
  - (ii)  $NaNO_3$
  - (iii)  $NH_4Cl$
  - (iv)  $KHSO_4$
- a. (ii), (iii), (iv)
  - b. (ii), (iii)
  - c. (iii), (iv)
  - d. (iii)

- 174.** Find the pH of 0.012 M solution of  $NH_4CN$  if  $K_a$  for  $HCN$  and  $K_b$  for  $NH_3$  are  $6.2 \times 10^{-10}$  and  $1.6 \times 10^{-5}$  respectively

- a. 8.2
- b. 9.2
- c. 4.8
- d. 5.8

- 175.** At 298 K the value of ionization constant of anilinium hydroxide is  $4.6 \times 10^{-10}$  and that of ionic product of water  $1 \times 10^{-14}$ , the value of degree of hydrolysis constant is nearly?

- a. 0.415 %
- b. 4.15 %
- c. 0.163 %
- d. 0.217 %

## Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given. Mark

- a. if A and R both are correct and R is the correct explanation of A;
- b. if A and R both are correct but R is not the correct explanation of A;
- c. A is true but R is false;
- d. A is false but R is true;
- e. A and R both are false.

176. (A): The pH of a buffer solution containing equal moles of acetic acid and sodium acetate is 4.8 (pKa of acetic acid is 4.8)
- (R): The ionic product of water at 25°C is  $10^{-14}$  mol<sup>2</sup> lit<sup>-2</sup>
177. (A): In the titration of Na<sub>2</sub>CO<sub>3</sub> with HCl using methyl orange indicator, the volume of the acid required at the equivalence point is twice that of the acid required using phenolphthalein indicator.
- (R): Two moles of HCl are required for complete neutralization of one mole of Na<sub>2</sub>CO<sub>3</sub>.
178. (A): Solubility of CaSO<sub>4</sub> in 0.1 M K<sub>2</sub>SO<sub>4</sub> is  $10^{-8}$  M hence its K<sub>sp</sub> is  $10^{-16}$
- (R): Since for CaSO<sub>4</sub> K<sub>sp</sub> = (s)<sup>2</sup>
179. (A): According to principle of common ion effect, the solubility of HgI<sub>2</sub> is expected to be less in an aqueous solution of KI than in water. But HgI<sub>2</sub> dissolves in an aqueous solution of KI to form a clear solution.
- (R): Iodide ion, I<sup>-</sup> is highly polarisable.
180. (A): On dissolving AgCl in 0.1 M solution of NaCl, CaCl<sub>2</sub> and NH<sub>3</sub> solution the solubility is lowest in NH<sub>3</sub>.
- (R): AgCl form complex with NH<sub>3</sub> in aqueous solution.
181. (A): The addition of a small amount of a ‘neutral’ electrolyte (one that does not share a common ion) such as NaCl to a dilute solution of acetic acid, will cause an increase in the degree of dissociation of the acid.
- (R): Due to the increased ionic strength, the mean ionic activity coefficient of H<sub>3</sub>O<sup>+</sup> and CH<sub>3</sub>COO<sup>-</sup> will increase.
182. (A): On addition of NH<sub>4</sub>Cl to NH<sub>4</sub>OH solution, pH decreases but remains greater than 7.
- (R): Addition of NH<sub>4</sub><sup>+</sup> ion decreases ionization of NH<sub>4</sub>OH thus, [OH<sup>-</sup>] is decreased, hence, pH decreases.
183. (A): The pH range of any indicator is from pK<sub>ln</sub> - 1 to pK<sub>ln</sub> + 1
- (R): As the pH of the indicator can be given as follows
- $$\text{pH} = \text{pK}_{\text{ln}} + \log \frac{(\text{ln}^-)}{(\text{Hln})}$$
- As pH range depends upon the ratio of [ln<sup>-</sup>] to [Hln] which can not have value 10 to 1/10 for all indicators.
184. (A): 0.33 M solution of KCN is more basic than 0.33 M solution of KF.
- (R): 0.33 M solution of KCN is more basic than 0.33 M solution of CH<sub>3</sub>COOK.
185. (A): On mixing equal volumes of 1M HCl and 2 M CH<sub>3</sub>COONa, an acidic buffer solution is formed.
- (R): Resultant mixture contains CH<sub>3</sub>COOH and CH<sub>3</sub>COONa which are parts of acidic buffer.
186. (A): H<sub>3</sub>PO<sub>3</sub> is a dibasic acid.
- (R): There are two hydrogen atoms directly attached to phosphorus
187. (A): Sodium carbonate can be titrated against sulphuric acid by using either phenolphthalein or methyl orange as indicator.
- (R): The volume of sulphuric acid required to produce colour change for the two indicators is different.
188. (A): A mixture of the solutions of a weak acid and its sodium salt acts as a good buffer.
- (R): The ratio of the salt to the acid in the mixture does not change substantially when small amount of acid or base is added to the buffer.
189. (A): pH of an amphiprotic anion always independent of concentration.
- (R): pH of amphiprotic anion can be given by  $\frac{1}{2} [\text{p}^{k1} + \text{p}^{k2}]$ . Here p<sup>k1</sup> and p<sup>k2</sup> are the dissociation constants of the acid in which amphiprotic anion is formed.
190. (A): In the volumetric estimation of iron (II) in acid solution in the presence of excess chloride by titration with permanganate solution, excess phosphoric acid and manganese (II) sulphate are added to the solution containing iron (II) before the titration.
- (R): Phosphoric acid complexes the iron (III) produced by the oxidation, and manganese (III) depresses the reduction potential of permanganate.
191. (A): When 0.1 M diprotic weak acid H<sub>2</sub>X dissociates with its dissociation constants K<sub>a1</sub> =  $10^{-4}$  and K<sub>a2</sub> =  $10^{-12}$ , then [X<sup>-2</sup>] is almost equal to  $10^{-12}$  M.
- (R): Since K<sub>a2</sub> << K<sub>a1</sub> for 0.1 M so H<sub>2</sub>X so [X<sup>-2</sup>] is negligible w.r.t. [HX<sup>-</sup>]. Hence [X<sup>-2</sup>]  $\approx$  K<sub>a2</sub>
192. (A): On mixing 500 mL of  $10^{-6}$  M Ca<sup>2+</sup> ion and 500 mL of  $10^{-6}$  MF<sup>-</sup> ion, the precipitate of CaF<sub>2</sub> will be obtained.
- K<sub>sp</sub> (CaF<sub>2</sub>) =  $10^{-18}$
- (R): If K<sub>sp</sub> is greater than ionic product, precipitate will be obtained.

### Matrix-Match Type Questions

193. Match the following:

**Column I (Titration)      Column II (Indication used)**

- A. Strong acid vs Strong base (p) Phenol phthalein
- B. Weak acid vs strong base (q) Methyl red
- C. Strong acid vs weak base (r) Methyl orange
- D. Weak acid vs weak base (s) No indicator

194. Match the following:

**Column I (Buffer)      Column II**

- A.  $\text{H}_2\text{CO}_3 + \text{NaHCO}_3$  (p) Removal of  $\text{PO}_4^{3-}$
- B.  $\text{CH}_3\text{COO}^- + \text{CH}_3\text{COONa}$  (q) Precipitate of hydroxides of  $\text{Fe}^{3+}, \text{Al}^{3+}, \text{Cr}^{3+}$
- C.  $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$  (r) Precipitate of Lead chromate
- D.  $\text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-}$  (s) Maintain pH of Blood

195. Match the following:

**Column I (Buffer)      Column II**

- A.  $1 \times 10^{-8}$  M KOH (p) 1.3
- B.  $1 \times 10^{-8}$  M HBr (q)  $\text{pH} = 6.95$
- C. 1 M HCl + 1 M NaOH (r)  $\text{pH} = 7.0414$
- D. 0.02 M  $\text{H}_2\text{SO}_4$  (s)  $\text{pH} = 7$   
(t) acidic solution

196. Match the effect of addition of 0.1 M NaOH to 0.1 M, 50 mL  $\text{H}_3\text{PO}_4$ .  $K_{\text{a}_1}, K_{\text{a}_2}, K_{\text{a}_3}$  are the I, II, III ionization constant of  $\text{H}_3\text{PO}_4$  respectively

**Column I (Buffer)      Column II**

- A. 150 mL of NaOH (p)  $\text{pH} = \text{p}K_{\text{a}_2}$
- B. 75 mL of NaOH (q)  $\text{pH} = \text{p}K_{\text{a}_1}$
- C. 25 mL of NaOH (r)  $\text{pH} = 7 + \frac{1}{2} [\text{p}K_{\text{a}_3} + \log C]$
- D. 100 mL of NaOH (s)  $\text{pH} = \frac{\text{p}K_{\text{a}_2} + \text{p}K_{\text{a}_3}}{2}$

197. Match the following:

**Column I      Column II**

- A.  $\text{CuSO}_4$  (p) Cationic interaction
- B.  $\text{Na}_2\text{CO}_3$  (q) Anionic interaction
- C.  $\text{FeCl}_3$  (r)  $\text{pH} > 7$
- D.  $\text{K}_2\text{SO}_4$  (s)  $\text{pH} < 7$   
(t) No ionic interaction

198. Match the following:

**Column I      Column II**

- A. Ostwald's dilution law (p)  $\alpha = \sqrt{K/C} = \sqrt{KV}$
- B. Ionic product (q)  $\frac{\text{No. of molecules dissociated}}{\text{Total No. of moles taken}}$
- C. Catalyst (r) Helps in attaining equilibrium at appropriate time.
- D. Degree of ionization (s)  $[\text{H}_3\text{O}^+] [\text{OH}^-]$   
(t) Increases with the increase of temperature

199. Match the following:

**Column I      Column II**

- A.  $\text{CCl}_4$  (p) Lewis acid
- B.  $\text{AlCl}_3$  (q) Lewis base
- C.  $\text{NH}_3$  (r) Bronsted acid
- D.  $\text{HClO}_4$  (s) Bronsted base  
(t) Neither lewis acid nor lewis base

200. Match the following:

**Column I      Column II**

- A. 0.5 M  $\text{NO}_3^- + 0.1 \text{ M NH}_4\text{OH}$  (p) 7
- B. 0.1 M KCl + 0.1 M  $\text{KNO}_3$  (q) greater than 7
- C. 0.2 M NaOH + 0.5 M  $\text{HCOOH}$  (r) between 1 to 7
- D. 0.1  $\text{NH}_4\text{Cl} + 0.1 \text{ M KOH}$  (s) 0.7

**The IIT-JEE Corner**

201. The solubility of  $A_2X_3$  is  $y$  mol dm $^{-3}$ . Its solubility product is

- a.  $6y^4$   
b.  $64y^4$   
c.  $36y^5$   
d.  $108y^5$

[IIT 1997]

202. If  $pK_b$  for fluoride ion at 25°C is 10.83, the ionization constant of hydrofluoric acid at this temperature is

- a.  $1.74 \times 10^{-5}$   
b.  $3.52 \times 10^{-3}$   
c.  $6.75 \times 10^{-4}$   
d.  $5.38 \times 10^{-2}$

[IIT 1997]

203. Which of the following statement is correct?

1. the pH of  $1.0 \times 10^{-8}$  M solution of HCl is 8
  2. the conjugate base of  $H_2PO_4^-$  is  $HPO_4^{2-}$
  3. autoprotolysis constant of water increases with temperature
  4. when a solution of a weak monoprotic acid is titrated against a strong base at half neutralization point,  $pH = (1/2) pK_a$ .
- a. 2, 3  
b. 1,2,3  
c. 3, 4  
d. 2,3,4

[IIT 1998]

204. A buffer solution can be prepared from a mixture of
1. sodium acetate and acetic acid in water
  2. sodium acetate and hydrochloric acid in water
  3. ammonia and ammonium chloride in water

205. ammonia and sodium hydroxide in water.

- a. 1,3,4  
b. 2,3,4  
c. 1,2,4  
d. 1,2,3

[IIT 1999]

206. The pH 0.1 M solution the following salts increases in the order

- a.  $NaCl < NH_4Cl < NaCN < HCl$   
b.  $HCl < NH_4Cl < NaCl < NaCN$   
c.  $NaCN < NH_4Cl < NaCl < HCl$   
d.  $HCl < NaCl < NaCN < NH_4Cl$

[IIT 1999]

207. For a sparingly soluble salt  $A_pB_q$ , the relationship of its solubility product ( $L_s$ ) with its solubility ( $S$ ) is

- a.  $L_s = S^{p+q} \cdot p^p \cdot q^q$   
b.  $L_s = S^{p+q} \cdot p^q \cdot q^p$

c.  $L_s = S^{pq} \cdot p^p \cdot q^q$

d.  $L_s = S^{pq} \cdot (pq)^{p+q}$

[IIT 2001]

208. Identify the correct order of solubility of  $Na_2S$ ,  $CuS$  and  $ZnS$  in aqueous medium

- a.  $Na_2S > CuS > ZnS$   
b.  $CuS > ZnS > Na_2S$   
c.  $Na_2S > ZnS > CuS$   
d.  $ZnS > Na_2S > CuS$

[IIT 2002]

209. Identify the correct order of solubility of  $Na_2S$ ,  $CuS$  and  $ZnS$  in aqueous medium

- a.  $Na_2S > CuS > ZnS$   
b.  $CuS > ZnS > Na_2S$   
c.  $Na_2S > ZnS > CuS$   
d.  $ZnS > Na_2S > CuS$

[IIT 2002]

210. A solution which is  $10^{-3}$  M each in  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Zn^{2+}$  and  $Hg^{2+}$  is treated with  $10^{-16}$  M sulphide ion. If  $K_{sp}$  of  $MnS$ ,  $FeS$ ,  $ZnS$  and  $HgS$  are  $10^{-15}$ ,  $10^{-23}$ ,  $10^{-20}$  and  $10^{-54}$  respectively, which one will precipitate first?

- a.  $MnS$   
b.  $FeS$   
c.  $ZnS$   
d.  $HgS$

[IIT 2003]

211. A weak acid  $HX$  has the dissociation constant  $1 \times 10^{-5}$  M. It forms a salt  $NaX$  on reaction with alkali. The degree of hydrolysis of 0.1 M solution of  $NaX$  is

- a. 0.1 %  
b. 0.01 %  
c. 0.0001 %  
d. 0.150 %

[IIT 2004]

212. When 0.1 mole of  $CH_3NH_2$  (ionization constant  $K_b = 5 \times 10^{-4}$ ) is mixed with 0.08 mol HCl and the volume is made up of 1 litre. Find the  $[H^+]$  of resulting solution.

- a.  $8 \times 10^{-2}$   
b.  $2 \times 10^{-11}$   
c.  $1.23 \times 10^{-4}$   
d.  $8 \times 10^{-11}$

[IIT 2005]

213.  $Ag^+ + NH_3 \leftrightarrow [Ag(NH_3)^+];$   
 $K_1 = 3.5 \times 10^{-3}$   
 $[Ag(NH_3)^+] + NH_3 \leftrightarrow [Ag(NH_3)_2]^+;$   
 $K_2 = 1.7 \times 10^{-3}$

Then the formation constant of  $[Ag(NH_3)_2]^+$  is

- a.  $6.08 \times 10^{-6}$   
b.  $6.08 \times 10^6$   
c.  $6.08 \times 10^{-9}$   
d. None

[IIT 2006]

- 214.** Solubility product constant ( $K_{sp}$ ) of salts of types MX,  $MX_2$  and  $M_3X$  at temperature 'T' are  $4.0 \times 10^{-8}$ ,  $3.2 \times 10^{-14}$  and  $2.7 \times 10^{-15}$ , respectively. Solubilities ( $\text{mol dm}^{-3}$ ) of the salts at temperature 'T' are in the order

- a.  $\text{MX} > \text{MX}_2 > \text{M}_3\text{X}$
- b.  $\text{M}_3\text{X} > \text{MX}_2 > \text{MX}$
- c.  $\text{MX}_2 > \text{M}_3\text{X} > \text{MX}$
- d.  $\text{MX} > \text{M}_3\text{X} > \text{MX}_2$

[IIT 2008]

- 215.** 2.5 mL of 2/5 M weak monoacidic base ( $K_{b1} \times 10^{-12}$  at 25°C) is titrated with 2/15 M HCl in water at

25°C. The concentration of  $\text{H}^+$  at equivalence point is ( $K_w = 1 \times 10^{-14}$  at 25°C)

- a.  $3.7 \times 10^{-13} \text{ M}$
- b.  $3.2 \times 10^{-7} \text{ M}$
- c.  $3.2 \times 10^{-2} \text{ M}$
- d.  $2.7 \times 10^{-2} \text{ M}$

[IIT 2008]

- 216.** The dissociation constant of a substituted benzoic acid at 25°C is  $1.0 \times 10^{-4}$ . The pH of a 0.01 M solution of its sodium salt is

- a. 6
- b. 8
- c. 7
- d. 4

[IIT 2009]

## ANSWERS

### Straight Objective Type Questions

- |       |       |       |       |       |       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1. c  | 2. a  | 3. c  | 4. d  | 5. d  | 6. c  | 7. d  | 8. c  | 9. a  | 10. c | 11. a | 12. b |
| 13. a | 14. a | 15. a | 16. a | 17. b | 18. b | 19. c | 20. b | 21. a | 22. b | 23. c | 24. a |
| 25. d | 26. d | 27. b | 28. b | 29. d | 30. c | 31. a | 32. d | 33. c | 34. b | 35. a | 36. d |
| 37. b | 38. c | 39. a | 40. b | 41. d | 42. c | 43. c | 44. b | 45. d | 46. d | 47. d | 48. d |
| 49. a | 50. b | 51. a | 52. a | 53. a | 54. c | 55. c | 56. c | 57. b | 58. d | 59. d | 60. d |
| 61. a | 62. b | 63. b | 64. b | 65. a | 66. b | 67. b | 68. b | 69. a | 70. c |       |       |

### Brainteasers Objective Type Questions

- |       |       |       |       |       |       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 71 c  | 72 a  | 73 a  | 74 d  | 75 c  | 76 a  | 77 a  | 78 b  | 79 b  | 80 c  | 81 c  | 82 b  |
| 83 c  | 84 a  | 85 d  | 86 c  | 87 c  | 88 d  | 89 a  | 90 c  | 91 d  | 92 c  | 93 a  | 94 b  |
| 95 b  | 96 a  | 97 a  | 98 a  | 99 a  | 100 d | 101 b | 102 c | 103 d | 104 a | 105 c | 106 a |
| 107 d | 108 a | 109 d | 110 d | 111 b | 112 b | 113 a | 114 d | 115 d | 116 d | 117 a | 118 b |
| 119 a | 120 c | 121 c | 122 a | 123 b | 124 a | 125 d | 126 b | 127 a | 128 a | 129 c | 130 b |

### Multiple Correct Answer Type Questions

- |              |              |              |              |              |              |                 |
|--------------|--------------|--------------|--------------|--------------|--------------|-----------------|
| 131. a, b, c | 132. a, c, d | 133. b, c, d | 134. a, c, d | 135. a, c, d | 136. c, d    | 137. a, b, d    |
| 138. b, c, d | 139. b, c    | 140. a, b, d | 141. b, c, d | 142. a, d    | 143. b, c    | 144. b, c, d    |
| 145. a, c    | 146. b, c, d | 147. b, c, d | 148. a, b, d | 149. a, d    | 150. b, c, d | 151. b, c       |
| 152. b, c, d | 153. a, c, d | 154. a, c, d | 155. a, b, c | 156. a, d    | 157. a, b, d | 158. a, b, c, d |
| 159. a, c, d | 160. a, c    |              |              |              |              |                 |

**Linked-Comprehension Type Questions****Comprehension 1**

161. a      162. d      163. c      164. a

**Comprehension 2**

165. b      166. c      167. a

**Comprehension 3**

168. c      169. a      170. b      171. a

**Comprehension 4**

172. d      173. c      174. b      175. a

**Assertion Reason Answers**

176 b      177 b      178 d      179 b      180 d

181 a      182 a      183 d      184 b      185 a

186 a      187 d      188 a      189 a      190 a

191 a      192 d

**Matrix-Match Type Questions**

193. A – (p, q, r), B – (p), C – (q, r), D – (s)

194. A – (s), B – (p, r), C – (q), D – (s)

195. A – (r), B – (q, t), C – (s), D – (p, t)

196. A – (r), B – (p), C – (q), D – (s)

197. A – (p, s), B – (q, r), C – (p, s), D – (t)

198. A – (p), B – (s, t), C – (r), D – (q, t)

199. A – (t), B – (p), C – (q, r, s), D – (r)

200. A – (s), B – (p), C – (r), D – (q)

**The IIT-JEE Corner**

201. d      202. c      203. a      204.      205. d      206. b      207. a      208. c      209. c

210. a      211. b      212. d      213. a      214.      215.      216. b

**Hints and Explanations**

1. For pure water,  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$

$$\text{K}_w = 10^{-6} \times 10^{-6} = 10^{-12}$$

2. Based have higher pH than acids; stronger is the base still higher is the pH.

$$W = Zit \quad (Z \text{ is the ECE})$$

3. Solubility product  $\propto$  solubility

PtS having least  $K_{\text{sp}}$  is least soluble here.

4. Among the given oxyacids HClO is the weakest as acidity depends on the oxidation state (+1 in HClO, which is lowest). Hence its conjugate base ( $\text{ClO}^-$ ) is the strongest one.

5.  $\text{OH}^- \leftrightarrow \text{H}^+ + \text{O}^{2-}$

Conjugate acid of  $\text{O}^{2-}$  ion is  $\text{OH}^-$ .

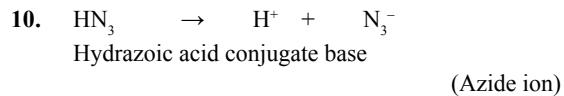
6. Molar conc. of HCl =  $10^{-8}$

$$\text{pH} = 8.$$

But this cannot be possible as pH of an acidic solution can not be more than 7. Here we have to consider  $[\text{H}^+]$  coming from  $\text{H}_2\text{O}$  to find Ph value.

7. Weak acid ( $\text{CH}_3\text{COOH}$ ) + its conjugate base ( $\text{CH}_3\text{COO}^-$  from  $\text{CH}_3\text{COONH}_4$ ) forms acid buffer

9. In molten state the cations and anions become free and flow of current is due to migration of these ions in opposite directions in the electric field.



11. Calculate the ionic product  $[\text{Ca}^{2+}][\text{F}^-]^2$  in each case and see that ionic product must exceed  $K_{\text{sp}}$  for pre-

- cipitation. Concentration of each ion is halved due to dilution effect
12.  $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$  precipitate radical of group III viz.,  $\text{Al}^{3+}$  and  $\text{Cr}^{3+}$
13. The equilibrium constant for the neutralization of a weak acid with a strong base can be given as,
- $$K = \frac{K_a}{K_w} = \frac{1.0 \times 10^{-4}}{1.0 \times 10^{-14}} = 1.0 \times 10^{10}$$
14.  $\text{H}_2\text{PO}_4^- \leftrightarrow \text{H}^+ + \text{HPO}_4^-$   
acid salt
15. Sn in  $\text{SnCl}_4$  has its octet completed while the central atoms in other molecules have incomplete octet.
17.  $\text{NH}_2^-$  (base) +  $\text{H}^+$   $\rightarrow$   $\text{NH}_3$  (conjugate acid)
19. The pH of the solution at the equivalence point is greater than 7 due to salt hydrolysis. So an indicator giving colour on the basic side will be suitable.
21. Gastric juice is acidic so the ionization of aspirin is suppressed whereas small intestine has basic medium therefore aspirin is more ionized.
23.  $\text{CH}_3\text{COONa}$  give basic solution as it is a salt of weak acid and strong base.
24. Weak base ( $\text{NH}_4\text{OH}$ ) + salt of a strong acid ( $\text{NH}_4\text{Cl}$ )
25. Solubility of hydroxide of group 2 elements increases down the group. Therefore  $\text{Be}(\text{OH})_2$  has lowest solubility and have lowest solubility product.
26. The corresponding acids are  
 a.  $\text{CH}_3\text{OH}$       b.  $\text{C}_2\text{H}_5\text{OH}$   
 c.  $(\text{CH}_3)_2\text{CHOH}$       d.  $(\text{CH}_3)_3\text{COH}$ .
- Among 1°, 2° and 3° alcohols, the order of acidity is 1° > 2° > 3°.
- As a weak acid has a strong conjugate base. Therefore (D) is the strongest conjugate base.
27.  $\text{NH}_4\text{OH} + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$
- $\text{NH}_4\text{Cl}$  is a salt of weak base and strong acid, so it gives the acidic solution with  $\text{pH} < 7$ .
28. This is according to Le–Chatelier's principle
29.  $\text{HCl} + \text{CH}_3\text{COOH} \leftrightarrow \text{Cl}^- + \text{CH}_3\text{COO}^-$   
Acid      Base      Conj. base      Conj. acid
30.  $\text{BF}_3$  and  $\text{SO}_3$  are Lewis acids because they can accept electron pairs.
31. In the Henderson's equation,  

$$\text{pH} = \text{pKa} + \log [\text{Salt}] / [\text{Acid}]$$
- when [Salt] = [Acid]  
 $\text{pH} = \text{pKa} = 9.30$
33. pH of blood remains same because it has a buffer solution of  $\text{H}_2\text{CO}_3 / \text{HCO}_3^-$ .
34. In a group of periodic table, there is a gradual increase in acid strength with an increase in atomic size.  
 As the order of atomic size of the given species is  $\text{F} < \text{Cl} < \text{Br} < \text{I}$ , therefore correct order of increasing acidity is  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ .
35. As  $\text{pH} = 3$   
 $\text{So } [\text{H}^+] = 1 \times 10^{-3}$   
 $\alpha = [\text{H}^+] / C$   
 $= 1 \times 10^{-3} / 0.1$   
 $= 0.01$   
 $\alpha \% = 1 \%$ .
36.  $(\text{Kh}) = \frac{\text{Kw}}{\text{Ka} \times \text{Kb}}$  .  
 $= \frac{1.0 \times 10^{-14}}{(4.0 \times 10^{-10}) \times (1.8 \times 10^{-5})} = 1.4$
37. Strength of HA =  $\sqrt{\text{K}_{\text{HA}}}$   
 Strength of HB =  $\sqrt{\text{K}_{\text{HB}}}$   
 $\frac{\sqrt{1 \times 10^{-3}}}{\sqrt{1 \times 10^{-5}}} = \sqrt{100} = 10$ .  
 Thus HA is ten times stronger than HB.
38.  $\text{HA}_1 / \text{HA}_2 = \sqrt{(\text{K}_{\text{A}_1} / \text{K}_{\text{A}_2})}$   
 $= \sqrt{(3.0 \times 10^{-4} / 1.8 \times 10^{-5})}$   
 $= \sqrt{(300 / 18)}$   
 $\approx 4 : 1$
39. According to the Bronsted–Lowry theory an acid is a substance which has a tendency to lose proton, while base is a substance which has a tendency to gain proton. Thus,  $\text{ClO}^-$  has maximum ability to gain proton, therefore  $\text{ClO}^-$  anion is the strongest Bronsted base.
40.  $\text{KCN}$  (aq)  $\leftrightarrow \text{K}^+ + \text{CN}^-$  and  
 $\text{CN}^- + \text{HOH} \leftrightarrow \text{HCN} + \text{OH}^-$   
 Since in this reaction, the pH will increase due to increase in  $\text{OH}^-$  ion concentration.
41. Solubility product of binary salt  $K_{\text{sp}} = S^2$   
 $= (2 \times 10^{-4})^2 = 4 \times 10^{-8}$ .

## 5.100 ■ Ionic Equilibrium

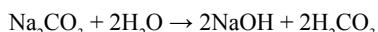
42.  $\text{MX}_2$  gives three ions after dissociation, thus it is ternary salt.

The solubility product of ternary salt ( $K_{\text{sp}}$ )  
 $= 4S^3 = 4 \times (0.5 \times 10^{-4})^3 = 5 \times 10^{-13}$

43.  $\text{PbCl}_2$  gives three ions after dissociation, therefore it is ternary salt.

The solubility of a ternary salt (S)  
 $= (\text{K}_{\text{sp}} / 4)^{1/3} = (1.5 \times 10^{-4} / 4)^{1/3}$   
 $= 3.34 \times 10^{-2} \text{ mol L}^{-1}$ .

44.  $\text{Na}_2\text{CO}_3$  is salt of weak acid  $\text{H}_2\text{CO}_3$  and strong base  $\text{NaOH}$ , therefore, has pH more than 7. Also, it dissociates to give two moles of  $\text{NaOH}$  (Alkaline solution).



45. In group III, addition of  $\text{NH}_4\text{Cl}$  increases  $\text{NH}_4^+$  ion concentration and decreases  $\text{OH}^-$  ion concentration produced from  $\text{NH}_4\text{OH}$  due to common ion effect.

46. As  $\text{pH} = 5$

$$\text{So } [\text{H}^+] = 1 \times 10^{-5}$$

$$\alpha = [\text{H}^+] / C$$

$$= 1 \times 10^{-5} / 0.005$$

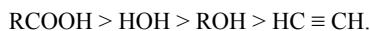
$$= 0.002$$

$$\text{so } \alpha \% = 0.2 \%$$

47. The higher value of  $\text{pKa}$  of a compound, lower is its strength.

The values of  $\text{pKa}$  for  $\text{CH}_3\text{COOH}$ , HOH,  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{HC} \equiv \text{CH}$  are 4.75, 15.7, 16 and 25 respectively.

The correct order of acidic strengths is



48. The concentration of  $[\text{H}^+] = C \times \alpha$

$$= 0.1 \times 0.02 = 2 \times 10^{-3} \text{ M.}$$

$$\text{concentration of } [\text{OH}^-] = \frac{\text{K}_w}{[\text{H}^+]} = \frac{1 \times 10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12} \text{ M.}$$

49. The rain water is generally pure. But when rain drops fall they dissolve various hazardous gases on the way, due to which their pH increases. And when rain is accompanied by thunderstorm the gases do not completely dissolve, because of high random momentum of gaseous molecules in air.

When rain is accompanied by thunderstorm, the collected rain water will have a pH value slightly lower than that of rain water without thunderstorm.

50.  $\text{pH} = -\log \sqrt{\text{K}_a} \times C$

$$5 = -\log \sqrt{\text{K}_a} \times 1$$

$$5 = -\frac{1}{2} \log \text{K}_a$$

$$\log \text{K}_a = -10$$

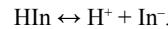
$$\text{K}_a = 10^{-10}$$

51. A buffer solution is prepared by mixing a weak acid with its salt of a strong base or by mixing a weak base with its salt of a strong acid.

Hence 0.05 M  $\text{KClO}_4$  and 0.05 M  $\text{HClO}_4$  are very dilute, therefore it is not a buffer solution.

52. The conjugate base is formed by the removal of  $\text{H}^+$  from acid i.e.,  $\text{H}_2\text{PO}_4^- \rightarrow \text{HPO}_4^{2-} + \text{H}^+$ . Thus  $\text{HPO}_4^{2-}$  is the conjugate base of  $\text{H}_2\text{PO}_4^-$ .

53. The dissociation reaction for acid is



Thus acid dissociation constant

$$(K_{\text{in}}) = \frac{[\text{H}^+] [\text{In}^-]}{[\text{HIn}]} \text{ or } [\text{H}^+] = K_{\text{in}} \times \frac{[\text{HIn}]}{[\text{In}^-]}$$

Taking logarithm on both sides,

$$\log \text{H}^+ = \log K_{\text{in}} + \log \frac{[\text{HIn}]}{[\text{In}^-]}$$

taking negative sign on both sides, we get

$$\text{pH} = \text{p}K_{\text{in}} + \log \frac{[\text{In}^-]}{[\text{HIn}]} \text{ or } \log \frac{[\text{In}^-]}{[\text{HIn}]} = \text{pH} - \text{p}K_{\text{in}}$$

54. NaOH is base and HCl is an acid, therefore their solutions in water become basic and acidic respectively. The value of ionic product of water does not change in acidic and basic solution. Thus ionic product of water remains same in these two solutions.

56.  $\text{MX}_4 \rightarrow \text{M}^{4+} \text{ (aq)} + 4\text{X}^- \text{ (aq)}$

The solubility product of  $\text{MX}_4$  ( $K_{\text{sp}}$ )

$$= S \times (4S)^4$$

$$K_{\text{sp}} = 256 \times S^5$$

$$S = (K_{\text{sp}} / 256)^{1/5}$$

60.  $\text{H}_2\text{S}$  being a weak acid does not dissociate appreciably in presence of HCl and thus  $[\text{S}^{2-}]$  becomes less due to common ion effect ( $\text{H}^+$ ).

61. As  $\text{pH} = 5$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-5} \text{ M}$$

$$M_1 = 10^{-5} \text{ let } V_1 = x$$

$$M_2 = ? V_2 = 100x$$

According to dilution law

$$M_1 V_1 = M_2 V_2$$

$$10^{-5} \times = M_2 100 x$$

$$\frac{10^{-5} x}{100 x} = M_2$$

$$= 10^{-7} M = M_2$$

$$[H_3O^+] = 10^{-7} M + 10^{-7} M$$

$$(\text{from water}) = 2 \times 10^{-7} M$$

$$pH = -\log [H_3O^+]$$

$$= -\log 2 \times 10^{-7} = 6.69$$

Hence, the solution becomes almost neutral

62.  $pOH = pK_b + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]}$

$$= 5 + \log_{10} \frac{0.02}{0.2} = 5 + (-1) = 4$$

$$pH = 14 - pOH$$

$$= 14 - 4 = 10$$

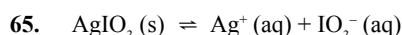
63.  $K_{sp} [AB] = [A^+] [B^-] = 10^{-8}$

$$\text{Putting } [A^+] = 10^{-3} M, \text{ we have } [B^-] = 10^{-5} M$$

AB will precipitate out if ionic product is greater than solubility product.

Thus precipitation  $[B^-] > 10^{-5} M$ .

64. As stronger the acid, weakest is the conjugate base. So decreasing order of basicity is



Let the solubility of  $AgIO_3$  be 'S'.

$$K_{sp} = [Ag^+] [IO_3^-]$$

$$1.0 \times 10^{-8} = S^2$$

$$S = 10^{-4} \text{ mol / litre}$$

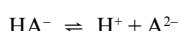
$$= \frac{10^{-4} \times 283}{1000} \times 100$$

$$= 283 \times 10^{-5}$$

$$= 2.83 \times 10^{-3} g / 100 ml$$

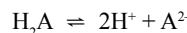


$$K_1 = \frac{[HA^-][H^+]}{[H_2A]} \quad \dots \dots \dots (1)$$



$$K_2 = \frac{[H^+] [A^{2-}]}{[HA^-]} \quad \dots \dots \dots (2)$$

For the reaction



$$K = \frac{[H^+]^2 [A^{2-}]}{[H_2A]} = K_1 \times K_2$$

$$= 1 \times 10^{-5} \times 5 \times 10^{-10}$$

$$= 5 \times 10^{-15}$$

67. For buffer solution

$$pH = pK_a + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]} .$$

$$= 4.5 + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]} .$$

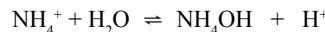
As HA is 50% is ionized so [salt] = [acid]

$$pH = 4.5$$

$$pH + pOH = 14$$

$$pOH = 14 - 4.5 = 9.5$$

68. If C is the initial concentration and 'x' is the degree of hydrolysis, then the degree of hydrolysis of  $NH_4Cl$ .



$$C(1-x) \qquad \qquad \qquad Cx \qquad \qquad Cx$$

$$K_h = \frac{Cx^2}{1-x} .$$

$$x = \sqrt{(K_h / C)} .$$

69.  $pH = 1$  means  $[H^+] = 10^{-1} M$ .

On adding equal amount of water  $[H^+] = 10^{-1} / 2$

$$pH = -\log_{10} (10^{-1} / 2) = 1 + \log_{10} 2$$

$$= 1 + 0.3 = 1.3$$

70. It is a salt of weak acid and weak base.

$$[H^+] = \sqrt{[(K_w \times K_a) / K_b]}$$

On solving, we get

$$pH = 7.01.$$

### Brainteasers Objective Type Questions

71. For a basic buffer,

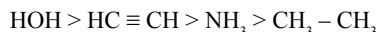
$$pH = 14 - pK_b - \log \frac{[\text{salt}]}{[\text{base}]}$$

$$= 14 - (-\log 10^{-10}) - \log 1$$

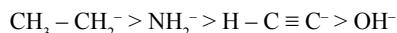
$$pH = 4$$

## 5.102 ■ Ionic Equilibrium

72. As the strength of conjugate base  $\propto$  1/acidic strength As acidic strength is



So



73.  $\frac{\text{Strength of HA}}{\text{Strength of HB}} = \frac{\sqrt{K_{HA}}}{\sqrt{K_{HB}}}$

$$\frac{\sqrt{3.2 \times 10^{-4}}}{\sqrt{2 \times 10^{-5}}} = \frac{\sqrt{32}}{\sqrt{2}} = \frac{\sqrt{16}}{\sqrt{1}} = \frac{4}{1}$$

i.e., strength of HA : strength of HB = 4 : 1

74.  $\text{MH}^+ = \frac{\text{M}_1 \text{V}_1 - \text{M}_2 \text{V}_2}{\text{V}_1 + \text{V}_2}$

$$= \frac{0.1 \times 75 - 0.2 \times 25}{100} = \frac{7.5 - 5.0}{100}$$

$$\text{MH}^+ = 2.5 / 100 = 2.5 \times 10^{-2} \text{ M}$$

$$= 2.5 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (2.5 \times 10^{-3})$$

$$= -1.398 + 3 = 1.602$$

i.e., in this case, pH is close to 1.

75.  $[\text{H}^+] = \frac{\text{K}_w}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{0.05} = 2 \times 10^{-13} \text{ mol L}^{-1}$

$$\text{pH} = -\log [\text{H}^+] = -\log [2 \times 10^{-13}]$$

$$= -\log 2 - \log 10^{-13} = -\log 2 - (-13) \log 10$$

$$= -0.3010 + (13 \times 1) = 12.7.$$

Hence the value of pH is greater than 7, thus the solution is basic.

76. Given : pH of first solution = 5

Or  $[\text{H}^+] = 10^{-5} \text{ M}$  and pH of second solution

$$= 3$$

$$\text{Or } [\text{H}^+] = 10^{-3} \text{ M}$$

On mixing the given solution, in equal volumes, the average hydrogen ion concentration  $[\text{H}^+]$

$$= \frac{10^{-5} + 10^{-3}}{2}$$

$$= 5.05 \times 10^{-4} \text{ M.}$$

$$\text{pH} = -\log_{10} [\text{H}^+] = -\log_{10} [5.05 \times 10^{-4}]$$

$$= -0.7033 - (-4) = 4 - 0.7033 = 3.2967$$

$$= 3.3.$$

77.  $M_R = \frac{M_1 V_1 + M_2 V_2}{\text{Total volume}}$

$$= \frac{0.2 \times 75 + 1 \times 25}{400} = 1 / 10$$

$$= 0.1$$

so net  $[\text{H}^+] = 0.1$  hence  $\text{pH} = 1$ .

78. The strength of acid ( $\text{pKa}$ ) =  $-\log (1.8 \times 10^{-5})$   
 $= 4.745$ .

According Henderson-Hasselbalch equation for acidic buffer that

$$\text{pH} = \text{pKa} + \log \frac{[\text{salt}]}{[\text{acid}]} = 4.745 + \log \frac{0.2}{0.15}$$

$$= 4.745 + \log 1.3333 = 4.745 + 0.125$$

$$= 4.87.$$

79. Solubility of  $\text{AgCl}$  (S) =  $\frac{\text{solubility of AgCl}}{\text{Mol. wt. of AgCl}}$

$$= \frac{1.435 \times 10^{-3}}{143.32} = 10^{-5} \text{ mol L}^{-1}$$

$\text{AgCl}$  gives two ions after dissociation, thus it is a binary salt.

The solubility product of a binary salt ( $\text{Ksp}$ ) =  $S^2 = (10^{-5})^2 = 10^{-10}$

80. Solubility product of  $\text{AgI}$  ( $\text{Ksp}$ ) =  $[\text{Ag}^+] [\text{I}^-]$

$$= 1.0 \times 10^{-16} \text{ mol}^2 \text{ L}^{-2}$$

and concentration of  $\text{KI} = 10^{-4} \text{ N}$

In  $10^{-4} \text{ N AgI}$ , concentration of iodide ion  $[\text{I}^-] = 10^{-4} \text{ N}$

The solubility product of  $\text{AgI}$  in  $10^{-4} \text{ N AgI}$  solution ( $\text{Ksp}$ ) =  $[\text{Ag}^+] [\text{Cl}^-]$

$$= (S) (S + 10^{-4}) \text{ (due to common ion effect)}$$

$$= (S) (10^{-4}) [\text{S} \lll 10^{-4}]$$

$$\text{or } 1.0 \times 10^{-16} = (S) (10^{-4})$$

$$S = \frac{1.0 \times 10^{-16}}{10^{-4}} = 1.0 \times 10^{-12}.$$

81.  $M_R = \frac{M_1 V_1 + M_2 V_2}{\text{Total volume}}$

$$= \frac{100 \times 0.015 + 100 \times 0.005}{200}$$

$$= 1 / 100$$

i.e.,  $[\text{H}^+] = 1/100 = 0.01$

so  $\text{pH} = 2$

82. Dissociation constant of glycine

$$(K) = K_{a_1} \times K_{a_2}$$

$$= (4.5 \times 10^{-3}) \times (1.7 \times 10^{-10}) = 7.65 \times 10^{-13}$$

the hydrogen ion concentration of glycine  $[H^+] = \sqrt{K_c}$

$$= \sqrt{(7.65 \times 10^{-13} \times 0.01)} = \sqrt{7.65 \times 10^{-15}}$$

$$= 0.87 \times 10^{-7} \text{ mol L}^{-1}$$

Therefore pH value of the glycine =  $-\log [H^+]$

$$= -\log [0.87 \times 10^{-7}] = 7 + 0.06 = 7.06$$

84. 50 ml of 0.1 M HCl =  $50 \times 0.1 = 5$  millimoles

$$50 \text{ ml of } 0.2 \text{ NaOH} = 50 \times 0.2 = 10 \text{ millimoles}$$

Millimoles of NaOH left after neutralization = 5

Volume of solution = 100 ml.

Molar conc. of NaOH

$$= \frac{5}{100} = 5 \times 10^{-2} \text{ M}$$

$$pOH = -\log_{10} (5 \times 10^{-2})$$

$$= \log_{10} \frac{1}{5 \times 10^{-2}} = \log_{10} 20 = 1.301$$

$$pH = 14 - 1.301 = 12.699 = 12.70.$$

$$85. 0.365 \text{ g HCl} = \frac{0.365}{36.5} \text{ mole} = 0.01 \text{ mole}$$

100 cm<sup>3</sup> of 0.2 M NaOH

$$= \frac{0.2}{1000} \times 100 = 0.02 \text{ mole}$$

NaOH left un-neutralised = 0.01 mole

Volume of solution = 100 ml

So molarity of NaOH in the solution

$$= \frac{0.01}{100} \times 1000 = 0.1 \text{ M} = 10^{-1} \text{ M}$$

$$\text{As } [H^+] = \frac{10^{-14}}{10^{-1} \text{ M}} = 10^{-13} \text{ M}$$

$$\text{So pH} = 13.$$

86. HCOOH / CH<sub>3</sub>COOH

$$= \sqrt{(K_a \text{ for formic acid} / K_a \text{ for acetic acid})}$$

$$= \sqrt{(1.77 \times 10^{-4} / 1.75 \times 10^{-5})}$$

$$= \sqrt{(10 / 1)}$$

$$= 3.178 / 1$$

$$= 3.178$$

87. K<sub>sp</sub> for Ag<sub>2</sub>SO<sub>4</sub> =  $[Ag^+]^2 [SO_4^{2-}]$

$[SO_4^{2-}]$  for precipitation of Ag<sub>2</sub>SO<sub>4</sub>

$$> \frac{K_{sp}}{[Ag^+]^2} = \frac{10^{-5}}{(0.1)^2} = 10^{-3} \text{ M}$$

Similarly,  $[SO_4^{2-}]$  for precipitation of BaSO<sub>4</sub>

$$> \frac{K_{sp}}{[Ba^{2+}]} = \frac{10^{-11}}{0.1} = 10^{-10} \text{ M}$$

$[SO_4^{2-}]$  for precipitation of CaSO<sub>4</sub>

$$> \frac{K_{sp}}{[Ca^{2+}]} = \frac{10^{-6}}{0.1} = 10^{-5} \text{ M}$$

So minimum  $[SO_4^{2-}]$  needed for precipitation is for BaSO<sub>4</sub>.

88. K<sub>sp</sub> for Mg(OH)<sub>2</sub> =  $[Mg^{2+}] [OH^-]^2$

$$10^{-12} = (0.01) [OH^-]^2$$

$$[OH^-]^2 = 10^{-10} \text{ M}$$

$$[OH^-] = 10^{-5} \text{ M}$$

$$[H^+] = 10^{-9} \text{ M}$$

$$\text{So pH} = 9.$$

89. 20 ml of 0.5 N HCl have  $20 \times 0.5$  milli eq. = 10 milli eq. of HCl

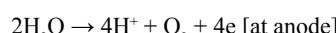
15 ml of 0.1 N NaOH have  $35 \times 0.1$  milli eq. = 3.5 milli eq. of NaOH

Thus 3.5 milli eq. of NaOH will neutralize 3.5 milli eq. of HCl

$$(10 - 3.5) = 6.5 \text{ milli eq of HCl will be left.}$$

Therefore solution will be acidic and it will turn methyl orange red.

90. The redox changes are



$$W / E = it / 96500$$

Eq. of K<sup>+</sup> lost = equivalent of H<sup>+</sup> formed

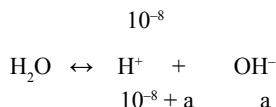
$$= \frac{it}{96500} = \frac{16.08 \times 10^{-3} \times 1 \times 60}{96500} = 10 \times 10^{-6}$$

$$[H^+] = \frac{10 \times 10^{-6}}{10^3} = 10 \times 10^{-9} = 10^{-8}$$

$$\text{pH} = 8.$$

91. HCl → H<sup>+</sup> + Cl<sup>-</sup>

## 5.104 ■ Ionic Equilibrium



$$K_w = [\text{H}^+] [\text{OH}^-]$$

$$10^{-14} = (10^{-8} + a) \times a$$

$$a = 0.95 \times 10^{-7}$$

$$[\text{H}^+] = 10^{-8} + 0.95 \times 10^{-7} = 1.05 \times 10^{-7}$$

92. According to Henderson–Hasselbalch equation

$$\text{pOH} = \text{pK}_b + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]}$$

At half stage of titration

$$[\text{Salt}] = [\text{Base}]$$

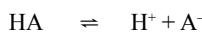
$$\text{pOH} = \text{pK}_b = 4.74$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14 - 4.74 = 9.26$$

93. As pH = 2

$$\text{So } [\text{H}^+] = 10^{-2} \text{ M}$$



$$C \text{ mol L}^{-1}$$

$$C(1-\alpha) \quad C\alpha \quad C\alpha$$

$$[\text{H}^+] = C\alpha$$

$$\alpha = [\text{H}^+] / C = 10^{-2} / 10^{-1}$$

$$= 10^{-1} = 0.1 \text{ M.}$$

94. At 25°C,  $\text{pK}_b$  for  $\text{NH}_3 = 4.7$  (in aq. solution)

$$[\text{NH}_4\text{Cl}] = 0.1 \text{ M} \text{ and } [\text{NH}_3] = 0.01 \text{ M}$$

For basic buffer,

$$\text{pOH} = \text{pK}_b + \log_{10} \frac{[\text{Conjugate acid B}^+]}{[\text{Weak base BOH}]}$$

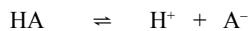
$$\text{pOH} = 4.7 + \log_{10} \frac{0.1}{0.01} .$$

$$= 4.7 + \log (10) = 5.7$$

$$\text{pH} + \text{pOH} = 14$$

$$\text{pH} = 14 - 5.7 = 8.3$$

95. Molar conc. of the given solution = 0.100 M



$$\text{Initial conc. } C \text{ mol L}^{-1}$$

$$\begin{array}{lll} \text{After diss.} & C - C\alpha & C\alpha \quad C\alpha \\ & & = C(1 - \alpha) \end{array}$$

$$K_a = \frac{C\alpha \cdot C\alpha}{C(1 - \alpha)} = \frac{C\alpha^2}{1 - \alpha} = C\alpha^2$$

$$\alpha = \sqrt{(K_a / C)}$$

$$= \sqrt{(1.0 \times 10^{-5}) / (0.1)} = 10^{-2}$$

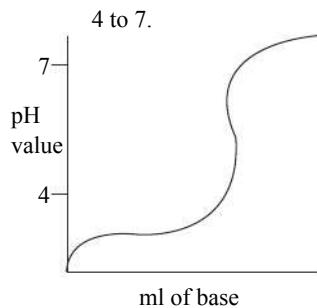
So % dissociation =  $10^{-2} \times 100 = 1\%$ .

96.  $\text{HCOONa}$ , being salt of weak acid and strong base, solution is basic.

$\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$ , being salt of weak acid and strong acid, solution is acidic.

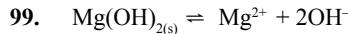
$\text{KCN}$ , being salt of strong base and weak acid, solution is basic.

97. pH curve of strong acid with a weak base is vertical over the pH range of



The indicator that shows colour change within this range is suitable. Methyl red (pH range 4.4–6.5) is the best choice.

98. Due to common ion effect of acetate ion further ionization of acetic acid is reduced, which leads to decrease in  $\text{H}^+$  concentration in solution, and hence increase in pH of the solution.



$$K_{sp} = \frac{[\text{Mg}]^{2+} [\text{OH}^-]^2}{[\text{Mg(OH)}_2]}$$

$$= 1.96 \times 10^{-11}$$

$$x \times (2x)^2 = 1.96 \times 10^{-11} \text{ (concentration of solid is unity)}$$

$$4x^3 = 1.96 \times 10^{-11}$$

$$x = \left( \frac{1.96 \times 10^{-11}}{4} \right)^{1/3}$$

$$x = (4.9 \times 10^{-11})^{1/3} = 1.6 \times 10^{-4}$$

$$\text{So, OH}^- \text{ concentration} = 2 \times 1.6 \times 10^{-4}$$

i.e.,  $[\text{OH}^-] = 3.2 \times 10^{-4}$

Now,  $\text{pOH} = -\log [\text{OH}^-]$

$$= -\log [3.2 \times 10^{-4}]$$

$$= 4 - 0.505 = 3.495$$

$$\text{As } \text{pH} = 14 - 3.495 = 10.505$$

101. No of milli equivalent of NaOH =  $30 \times 1 = 30$

$$\text{No of milli equivalent of HCl} = 50 \times 1 = 50$$

$$\text{As, NO of milli equivalent of HCl left after titration} \\ = 50 - 30 = 20$$

$$\text{Total volume of the mixture} = 50 + 30 = 80$$

i.e., 20 milli equivalent or 0.02 equivalent of HCl are present in 80 ml.

So, 250 milli equivalent or 0.25 equivalent of HCl are present in 1000 ml or 1 litre.

i.e., 0.025 N HCl  $\approx$  0.25 M NaOH (Monobasic)

$$\text{So, } [\text{H}^+] = 0.25 \text{ M}$$

$$\text{pH} = -\log_{10} [0.25]$$

$$\text{pH} = -\log_{10} [2.5 \times 10^{-1}]$$

$$\text{pH} = 1 - \log_{10} 2.5$$

$$\text{pH} = 1 - 0.3979$$

$$\text{pH} = 0.6021$$

102. pH of buffer is

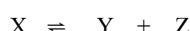
$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

Since, [salt] = [acid], pH = pK<sub>a</sub>

103. Equimolar solutions of the given chlorides when prepared in water forms their respective hydroxides. Be(OH)<sub>2</sub> is amphoteric, but the hydroxides of other alkaline earth metals are basic. The basic strength increases down the group. Therefore higher the basic character higher will be the pH.

104. X = Y + Z .....(i)

- A = 2B .....(ii)

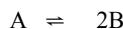


$$\text{Initially} \quad 1 \quad 0 \quad 0$$

$$\text{At. eq.} \quad 1 - \alpha \quad \alpha \quad \alpha$$

Total No. of moles at equilibrium

$$= 1 - \alpha + 2\alpha = 1 + \alpha$$



Initially, when t = 0	1	0
At. eq.	$1 - \alpha$	$2\alpha$

Total no. of moles at equilibrium

$$= 1 - \alpha + 2\alpha = 1 + \alpha$$

$$K_{p_1} = \frac{P_Y \times P_Z}{P_X}$$

$$= \frac{[(\alpha / 1 + \alpha) P_1] [(\alpha / 1 + \alpha) \times P_1]}{[1 - \alpha / 1 + \alpha] \times P_1}$$

$$K_{p_2} = (P_B)^2 = \frac{[(2\alpha / 1 + \alpha) \times P_2]^2}{[1 - \alpha / 1 + \alpha] \times P_2}$$

$$\frac{K_{p_1}}{K_{p_2}} = \frac{P_1}{4P_2}$$

$$\frac{P_1}{P_2} = \frac{36}{1} = 36 : 1$$

$$105. A_x B_y \rightleftharpoons xA^y + yB^{x-}$$

$$C \quad 0 \quad 0 \quad (\text{Initially})$$

$$C(1 - \alpha) \quad Cx\alpha \quad Cy\alpha \quad (\text{At equilibrium})$$

$$\text{As } K_{eq} = \frac{(Cx\alpha)^x (Cy\alpha)^y}{C(1 - \alpha)}$$

For concentrated solution of weak electrolyte,  $\alpha$  is very small. Therefore,  $(1 - \alpha) \approx 1$ .

$$\text{So, } \alpha = \left( \frac{K_{eq}}{C^{x+y-1} \cdot x^x \cdot y^y} \right)^{\frac{1}{x+y}}$$

$$106. \text{Solubility of BaSO}_4 (\text{S}) = \frac{\text{solubility of BaSO}_4}{\text{Mol. wt. of BaSO}_4} \\ = \frac{2.33 \times 10^{-3}}{233} = 0.01 \times 10^{-3} \text{ mol L}^{-1}$$

BaSO<sub>4</sub> gives two ions after dissociation, thus it is a binary salt.

$$(K_{sp}) = S^2 = (0.01 \times 10^{-3})^2 = (1 \times 10^{-5})^2 \\ = 1 \times 10^{-10}$$

$$109. S_{\text{CuS}} = (10^{-37})^{1/2} = 10^{-18.5};$$

$$S_{\text{HgS}} = (10^{-54})^{1/2} = 10^{-27}$$

$$K_{sp} \text{ of Ag}_2\text{S} = 4S^3 = 10^{-49}$$

$$S^3 = \frac{10^{-49}}{4} = 0.025 \times 10^{-48}$$

$$S = 0.292 \times 10^{-16}$$

Thus Ag<sub>2</sub>S > CuS > HgS.

$$110. \text{pH} = -\log_{10} [\text{H}^+]$$

$$[\text{H}^+] = 10^{-\text{pH}}$$

## 5.106 ■ Ionic Equilibrium

$$[\text{H}^+] \text{ of solution 1} = 10^{-3}$$

$$[\text{H}^+] \text{ of solution 2} = 10^{-4}$$

$$[\text{H}^+] \text{ of solution 3} = 10^{-5}$$

Total concentration of  $[\text{H}^+]$

$$= 10^{-3} (1 + 1 \times 10^{-1} + 1 \times 10^{-2})$$

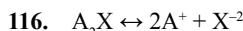
$$= 10^{-3} \left( \frac{1}{1} + \frac{1}{10} + \frac{1}{100} \right)$$

$$= 10^{-3} \left( \frac{111}{100} \right) = 1.11 \times 10^{-3}$$

Therefore,  $\text{H}^+$  ion concentration in mixture of equal volume of these acid solutions

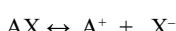
$$= \frac{1.11 \times 10^{-3}}{3} = 3.7 \times 10^{-4} \text{ M}$$

113. Here the correct order is IV < II < III < I.



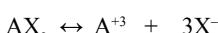
$$\text{K}_{\text{sp}} = (2\text{S})^2 (\text{S}) = 4\text{S}^3$$

$$\text{S} = [\text{K}_{\text{sp}}/4]^{1/3}$$



$$\text{K}_{\text{sp}} = (\text{S}_1)^2$$

$$\text{S}_1 = (\text{K}_{\text{sp}})^{1/2}$$



$$\text{K}_{\text{sp}} = (\text{S}_2)(3\text{S}_2)^3 = 27\text{S}_2^4$$

$$\text{S}_2 = [\text{K}_{\text{sp}} / 27]^{1/4}$$

Thus, it is clear that  $\text{S}_1 > \text{S} > \text{S}_2$

121. Acidic strength of oxyacids increases with increase in electronegativity of the non-metal and its oxidation number. thus the order is



123. Solution of I is acidic ( $\text{pH} < 7$ ), solution of II is basic ( $\text{pH} > 7$ ), solution of III is neutral ( $\text{pH} = 7$ ) while solution of IV is strongly basic ( $\text{pH} >> 7$ ).

Thus the order of pH is IV > II > III > I

124.  $\text{P}_3\text{Q}_2(\text{s}) \leftrightarrow 3\text{P}^{2+} + 2\text{Q}^{3-}$ .

Solubility =  $\times / \text{M mol lit}^{-1}$

$$[\text{P}^{2+}] = \frac{3x}{M} \text{ mol lit}^{-1}; [\text{Q}^{3-}] = \frac{2x}{M}$$

$$\text{K}_{\text{sp}} = (3x/M)^3 (2x/M)^2 = 108 x^5 / M^5$$

$$\frac{[\text{Q}^{3-}]}{\text{K}_{\text{sp}}} = \frac{2x}{M} \cdot \frac{M^5}{108 x^5} = \frac{1}{54} \frac{M^4}{x^4} .$$

$$127. \quad \text{pOH} = \text{pK}_b + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]} .$$

$$= -\log_{10} (1.5 \times 10^{-9}) + \log_{10} \frac{0.15}{500 \times 0.2 \times 10^{-3}} .$$

$$= 9 - \log_{10} 1.5 + \log_{10} 1.5 = 9$$

$$\text{pH} = 14 - 9 = 5.$$

$$130. \quad [\text{H}^+] = \frac{\text{remaining mili eq. of H}^+}{\text{total volume (in mL)}}$$

$$= \frac{40}{100} = \frac{4}{10}$$

$$\text{Hence pH} = 1 - \log 4 = 1 - 0.6$$

$$= 0.4$$

### Multiple Correct Answer Type Questions

135. The  $10^{-8} \text{ M}$  solution of HCl is very dilute.

And the contribution of  $\text{H}^+$  ions, due to self ionization of water, cannot be neglected. Therefore,  $[\text{H}^+]_{\text{total}} = [\text{H}^+] \text{ (from HCl + water)} = 10^{-8} + 10^{-7} = 10^{-7} (10^{-1} + 1)$

$$= 10^{-7} (0.1 + 1) = 10^{-7} \times 1.1.$$

$$\text{pH} = -\log[\text{H}^+] = -\log (1.1 \times 10^{-7}) = 6.96.$$

So option (B) is not true, while rest are true.

143. pH of  $10^{-8} \text{ M}$  HCl is not 8 but it is less than 7 because in this case contribution of  $\text{H}^+$  from water can not be neglected.

So total  $\text{H}^+ = 10^{-8} \text{ (from acid)} + 10^{-7} \text{ (from water)}$

$$= 10^{-8} (1 + 10)$$

$$= 11 \times 10^{-8} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log [11 \times 10^{-8}]$$

$$= -[\log 11 + \log 10^{-8}]$$

$$= -[1.0414 - 8]$$

$$= 6.9586 \simeq 6.96$$

154.  $\text{CH}_3\text{COOH}$  is weak acid while  $\text{NaOH}$  is strong base, so one equivalent of  $\text{NaOH}$  can not be neutralized with one equivalent of  $\text{CH}_3\text{COOH}$ . Therefore the solution of one equivalent of each does not have pH value as 7. That is it is incorrect

160. As  $\text{KOH}, \text{HNO}_3$  are limiting reagents here.

166. suppose the concentration of the acetate salt added is  $x$  times the concentration of acetic acid solution of obtain pH = 7. Then  $[\text{CH}_3\text{COO}^-]$

$$= x \times [\text{CH}_3\text{COOH}]$$

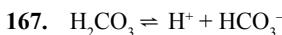
$$\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = x$$

Now, for acid buffer,  $\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$

$$7 = -\log(1.8 \times 10^{-5}) + \log x$$

$$7 = 4.76 + \log x \text{ or } \log x = 2.24$$

$$x = 1.73 \times 10^2 = 173 \text{ times}$$



$$K_1 = \frac{[\text{H}^+] [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{K_1}{[\text{H}^+]}$$

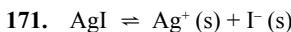
$$\text{pH} = 7.40 \text{ means } -\log [\text{H}^+] = 7.4$$

$$\text{or } \log [\text{H}^+] = -7.4 = 8.6$$

$$[\text{H}^+] = 3.981 \times 10^{-8}$$

$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{4.5 \times 10^{-7}}{3.981 \times 10^{-8}}$$

$$= 11.3$$



$$K_{\text{sp}} = S^2$$

$$S = \sqrt{(K_{\text{sp}})} = \sqrt{(4.9 \times 10^{-11})} = \sqrt{(49 \times 10^{-12})}$$

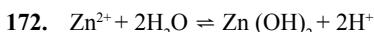
$$= 7 \times 10^{-6}$$

In 0.001 M KI,

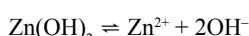
$$K_{\text{sp}} = (7 \times 10^{-6})(7 \times 10^{-6})(10^{-2})$$

$$= 49 \times 10^{-14}$$

$$S = \sqrt{K_{\text{sp}}} = \sqrt{(49 \times 10^{-14})} = 7.0 \times 10^{-7}$$

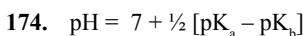


$$K_h = \frac{[\text{Zn(OH)}_2][\text{H}^+]^2}{[\text{Zn(OH)}_2]^2}$$



$$K_b = \frac{[\text{Zn}^{2+}][\text{OH}^-]^2}{[\text{Zn(OH)}_2]}$$

$$= \text{Hence } K_h = \frac{K_w^2}{K_b}$$



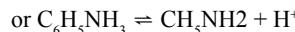
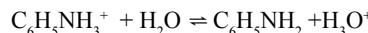
$$= 7 + \frac{1}{2} [\log K_a + \log K_b]$$

$$= 7 + \frac{1}{2} [-\log(6.2 \times 10^{-10}) + \log(1.6 \times 10^{-5})]$$

$$= 7 + \frac{1}{2} [(10 - 0.7924) + (-5 + 0.2041)]$$

$$= 9.21$$

175. Aniline hydrochloride ( $\text{C}_6\text{H}_5\text{NH}_3^+$ ) is a salt of weak base ( $\text{C}_6\text{H}_5\text{NH}_2$ ) and strong acid (HCl) so for it



$$K_h = \frac{K_w}{K_b} = \frac{1.02 \times 10^{-14}}{5.93 \times 10^{-10}}$$

$$= 1.72 \times 10^{-5}$$

$$h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{1.72 \times 10^{-5}}{10}}$$

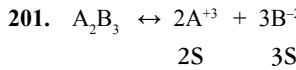
$$= 4.15 \times 10^{-3}$$

$$= 4.15 \times 10^{-3} \times 100\% = 0.415\%$$

184. As  $\text{CN}^-$  is more basic than  $\text{F}^-$  and  $\text{CH}_3\text{COO}^-$

187. It can be titrated only by basic nature indicator.

190. Both assertion and reason is correct and give correct explanation.



$$K_{\text{sp}} = [\text{A}^{+3}]^2 [\text{B}^{-2}]^3 = (2\text{S})^2 (3\text{S})^3$$

$$K_{\text{sp}} = 108 \text{ S}^5$$

202.  $\text{pK}_a = 14 - \text{pK}_b = 14 - 10.83 = 3.17$

$$\text{Ka} = \text{Antilog}(-\text{pK}_a)$$

$$\text{Ka} = \text{Antilog}(-3.17) = 6.75 \times 10^{-4}$$

203. pH of  $10^{-8}$  M HCl is not 8 but it is less than 7.

Only choices 2, 3 are correct.

205. In all the 1, 2, 3 buffer solution is prepared. In choice 2, when  $\text{CH}_3\text{COONa}$  reacts with HCl it forms  $\text{CH}_3\text{COOH} + \text{NaCl}$ .

206. HCl : Strong acid

$\text{NH}_4\text{Cl}$  : Salt of weak base + strong acid → it gives acidic solution.

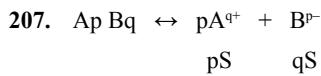
$\text{NaCl}$  : Salt of strong base + strong acid → it gives neutral solution with  $\text{pH} = 7$ .

$\text{NaCl}$  : Salt of strong base + weak acid → it gives basic solution with  $\text{pH} > 7$ .

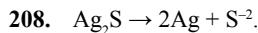
Thus the increasing order of pH is

$\text{HCl} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{NaCN}$

## 5.108 ■ Ionic Equilibrium



$$\begin{aligned}\text{K}_{\text{sp}} \text{ or } \text{L}_s &= [\text{A}^{q+}]^p \cdot [\text{B}^{p-}]^q \\ &= (\text{pS})^p \cdot (\text{qS})^q = \text{p}^p \cdot \text{S}^p \cdot \text{q}^q \cdot \text{S}^q \\ \text{L}_s &= \text{S}^{p+q} \cdot \text{p}^p \cdot \text{q}^q\end{aligned}$$



Solubility product of this reaction

$$(\text{K}_{\text{sp}}) = [\text{Ag}]^2 [\text{S}^{2-}]$$

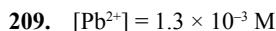
solubility of each product is S, then solubility product ( $\text{K}_{\text{sp}}$ ) =  $(2S)^2 \times (S)$

$$256 \times 10^{-6} = 4S^2 \times S$$

$$256 \times 10^{-6} = 4S^3$$

$$S^3 = \frac{256 \times 10^{-6}}{4} = 64 \times 10^{-6}$$

$$S = \sqrt[3]{(64 \times 10^{-6})} = 4 \times 10^{-2}$$



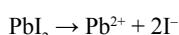
$$[\text{I}^-] = 2 \times 1.3 \times 10^{-3} \text{ M}$$

$$= 2.6 \times 10^{-3} \text{ M}$$

$$\text{K}_{\text{sp}} = [\text{Pb}^{2+}] [\text{I}^-]^2$$

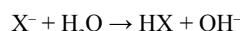
$$= (1.3 \times 10^{-3}) (2.6 \times 10^{-3})^2$$

$$= 8.8 \times 10^{-9}$$



210. The one with lowest value of  $\text{K}_{\text{sp}}$ , i.e.,  $\text{HgS}$  will precipitate out first.

211. Hydrolysis reaction is



For a salt of weak acid and strong base

$$\text{As } K_h = \frac{K_w}{K_a} = ch^2$$

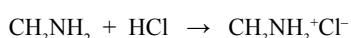
$$\frac{10^{-14}}{10^{-5}} = 0.1 \times h^2$$

$$h^2 = 10^{-8}$$

$$h = 10^{-4}$$

$$\text{So \% hydrolysis} = 10^{-4} \times 100 = 10^{-2} = 0.01$$

212.  $\text{CH}_3\text{NH}_2$  (base) on reaction with  $\text{HCl}$  (acid) to give a salt of weak base and strong acid as  $\text{CH}_3\text{NH}_3^+\text{Cl}^-$ .



$$\text{At } t = 0 \quad 0.1 \text{ mole} \quad 0.08 \text{ mole} \quad 0$$

After reac.  $(0.1 - 0.08) = 0.02 \text{ mole}$   
 $0.08 \text{ mole}$

So, it acts as basic buffer solution due to presence of base and salt is solution of one litre.

$$\text{pOH} = -\log_{10} K_b + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]} .$$

$$= -\log_{10} K_b + \log_{10} \frac{[\text{CH}_3\text{NH}_3^+\text{Cl}^-]}{[\text{CH}_3\text{NH}_2]}$$

$$= -\log_{10} 5 \times 10^{-4} + \log_{10} \frac{[0.08]}{[0.02]}$$

$$= -\log_{10} 5 + 4 \log_{10} 10 + \log_{10} \frac{[0.08]}{[0.02]}$$

$$= -0.699 + 4 + 0.602 = 3.9030$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14 - 3.903 = 10.097$$

$$10.097 = -\log_{10} [\text{H}^+]$$

$$[\text{H}^+] = 8.0 \times 10^{-11}$$



$$k_1 = 3.5 \times 10^{-3}$$



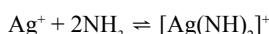
$$k_2 = 1.7 \times 10^{-3}$$

According to these reactions

$$k_1 = \frac{[\text{Ag}(\text{NH}_3)]^+}{[\text{Ag}^+] [\text{NH}_3]} \quad \dots \dots \text{(i)}$$

$$k_2 = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}(\text{NH}_3)]^+ [\text{NH}_3]} \quad \dots \dots \text{(ii)}$$

For the formation of  $[\text{Ag}(\text{NH}_3)]^+$



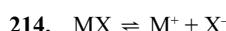
Formation constant ( $K$ )

$$= \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+] [\text{NH}_3]^2} \quad \dots \dots \text{(iii)}$$

From equation (i) and (ii)

$$K = k_1 \times k_2$$

$$= 3.5 \times 10^{-3} \times 1.7 \times 10^{-3}$$



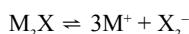
$$\text{Solubility of MX} (s_1) = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4}$$



$$\text{Solubility of } \text{MX}_2(s_2) = 4s_2^3 = K_{\text{sp}}$$

$$s_2 = \left( \frac{K_{\text{sp}}}{4} \right)^{1/3} = \left( \frac{3.2 \times 10^{-14}}{4} \right)^{1/3}$$

$$= 2 \times 10^{-5}$$



$$\text{Solubility of } \text{M}_3\text{X}(s_3) = 27s_3^4$$

$$= 2.7 \times 10^{-15}$$

$$= s_3 = 10^{-4}$$

$$s_1 > s_3 > s_2$$



For titration

$$N_{\text{acid}} \times V_{\text{acid}} = N_{\text{base}} \times V_{\text{base}}$$

$$\frac{2}{15} \times V = 2.5 \times \frac{2}{5}$$

Hence V = volume of HCl used = 7.5 mL.

In resulting solution,

Concentration of salt [BCl]

$$= \frac{2}{5 \times 2.5/10} = \frac{2}{20} = 0.1$$

$$\text{As } \frac{\text{Ch}^2}{1-h} = \frac{K_w}{K_b}$$

$$\text{or } h = \sqrt{\frac{K_w}{K_b \times C}} = \sqrt{\frac{10^{-14}}{10^{-12} \times 0.1}}$$

$$\text{So } h = \sqrt{\frac{1}{10}}$$

Now, as  $[\text{H}^+] = \text{Ch}$

$$= 0.1 \times \sqrt{\frac{1}{10}}$$

$$= 0.1 \times 0.316$$

$$= 3.16 \times 10^{-2} \text{ M}$$

$$\text{So } [\text{H}^+] \approx 3.2 \times 10^{-2}$$

## Numericals for Practice

- 20 ml 0.5 M solution of a weak acid HA and 20 ml 1.0 M HCl are mixed together. 1.2 g NaOH of them dissolved into it. If pH of the resulting solution is 5.5, pKa of the weak acid is
  - 4.8
  - 5.2
  - 9.0
  - 7
- The pKa of HCN is 9.30. The pH of a solution prepared by mixing 1.5 moles of KCN and 1.5 moles of HCN in water and making up the total volume to 500 ml is
  - 7.0
  - 4.7
  - 8.3
  - 9.3
- The formation constant of the complex  $[\text{Ag}(\text{NH}_3)_2]^+$  at 25°C is  $1.0 \times 10^8$ . In a solution prepared by mixing  $1.0 \times 10^{-3}$  mole of  $\text{AgNO}_3$  and 1.0 lit of 0.1 M  $\text{NH}_3$  solution, the  $[\text{Ag}^+]$  is about
  - $1.0 \times 10^{-10} \text{ M}$
  - $1.0 \times 10^{-8} \text{ M}$
  - $1.0 \times 10^{-9} \text{ M}$
  - $10.6 \times 10^{-8} \text{ M}$
- The solubility of calcium arsenate in pure water at 25°C is  $9.0 \times 10^{-5}$  mol/lit. The solubility product,  $K_{\text{sp}}$  at this temperature is

- $6.4 \times 10^{-19}$
- $7.6 \times 10^{-19}$
- $6.4 \times 10^{19}$
- $6.4 \times 10^{-20}$

- The solubility product values of barium sulphate and barium carbonate are  $1.0 \times 10^{-10}$  and  $5.0 \times 10^{-9}$  respectively. When the two salts are equilibrated in pure water the ratio of  $[\text{SO}_4^{2-}] / [\text{CO}_3^{2-}]$  is
  - 0.05
  - 0.02
  - 0.002
  - 0.01
- The solubility product of  $\text{Ag}_2\text{CrO}_4$  at 25°C is  $1.686 \times 10^{-12}$ . The  $[\text{Ag}^+]$  in a solution of 0.02 M  $\text{Na}_2\text{CrO}_4$  is
  - $4.56 \times 10^{-5} \text{ M}$
  - $4.56 \times 10^{-6} \text{ M}$
  - $9.1 \times 10^{-6} \text{ M}$
  - $9.1 \times 10^{-5} \text{ M}$
- A buffer solution is prepared by mixing 0.02 M benzoic acid solution and sodium benzoic solution to give a pH of 5.4.  $K_a$  of benzoic acid =  $6.4 \times 10^{-5}$ . The proportion,  $[\text{acid}] / [\text{salt}]$  in which the two solutions have to be mixed is
  - 1.0
  - 0.5
  - 0.3
  - 0.7

## 5.110 ■ Ionic Equilibrium

8. In a saturated solution of silver chromate in pure water at 25°C, the concentration of chromate ion is  $2 \times 10^{-4}$  mol.lit<sup>-1</sup>. The solubility product of silver chromate is  
a.  $3.2 \times 10^{-10}$       b.  $3.2 \times 10^{-11}$   
c.  $4 \times 10^{-8}$       d.  $2.3 \times 10^{-12}$
9. The approximate pH of a saturated solution of H<sub>2</sub>S in water ( $[H_2S] = 0.1$  M) at 25°C is ( $K_1$ , H<sub>2</sub>S =  $1.0 \times 10^{-7}$ ,  $K_2$ , H<sub>2</sub>S =  $1.3 \times 10^{-13}$ )  
a. 3.0      b. 4.0  
c. 5.0      d. 2.0
10. 25.0 ml of 0.05 M H<sub>2</sub>SO<sub>4</sub> is added to 0.10 M NaOH solution. The resulting solution has a pH of 10.6. The volume of NaOH solution taken is  
a. 25.0 ml      b. 25.1 ml  
c. 25.2 ml      d. 25.52 ml
11. The degree of hydrolysis of 0.10 M aniline acetate (aq) is ( $K_a = 1.75 \times 10^{-5}$  and  $K_b = 4.0 \times 10^{-10}$ )  
a. 0.3484      b. 0.9564  
c. 0.4584      d. 0.5444
12. Assume the ionic product of water to be  $10^{-14}$  at a certain temperature. The dissociation constant of water (in mol lit<sup>-1</sup>) at the same temperature is roughly  
a.  $3.6 \times 10^{-17}$       b.  $1.8 \times 10^{-16}$   
c.  $8.1 \times 10^{-16}$       d.  $10^{-16}$
13. What is the minimum pH range over which an acid-base indicator HIn ( $K_{In} = 10^{-5.5}$ ) may be effectively used, if the colour is distinctly discernable, when the concentration ratio  $[In^-] / [HIn]$  is  $\geq 10$  or  $\leq 0.1$ ?  
a. 4.5 to 6.5      b. 4.0 to 6.0  
c. 5.0 to 6.0      d. 5.5 to 6.5
14. Blood is buffered with CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup>. What is the ratio of the base concentration to the acid (i.e., CO<sub>2</sub> (aq.) + H<sub>2</sub>CO<sub>3</sub>) concentration to maintain the pH of blood at 7.4? The first dissociation constant of H<sub>2</sub>CO<sub>3</sub> (H<sub>2</sub>CO<sub>3</sub>  $\leftrightarrow$  H<sup>+</sup> + HCO<sub>3</sub><sup>-</sup>) is  $4.2 \times 10^{-7}$  where the H<sub>2</sub>CO<sub>3</sub> is assumed to include CO<sub>2</sub> (aq) i.e., dissolved CO<sub>2</sub>.  
a. 1.06      b. 10.6  
c. 108      d. 106
15. The first and the second dissociation constants of H<sub>2</sub>S are respectively  $10^{-7}$  and  $10^{-14}$  (approximate). The pH of a 0.1 M H<sub>2</sub>S solution is roughly  
a. 2.0      b. 3.0  
c. 3.5      d. 4.0
16. Two weak monobasic acids HA and HB have dissociation constants  $4 \times 10^{-6}$  and  $1 \times 10^{-8}$  respectively. The hydrogen ion concentration ratio for HA and HB is roughly  
a. 5 : 1      b. 20 : 1  
c. 100 : 1      d. 400 : 1
17. pH of the solution prepared by mixing 5ml of N/10 CH<sub>3</sub>COOH and 5 ml of N/10 NaOH solution is (Assume the Ka of CH<sub>3</sub>COOH is  $10^{-5}$ )  
a. 7      b. 5.16  
c. 1.3      d. 8.84
18. How many times (approximately) should an extremely weak monobasic acid, HA, be diluted, so that the hydrogen ion concentration is reduced to  $\frac{1}{4}$  of that in the original solution?  
a. 2      b. 4  
c. 8      d. 16
19. In an acid-base titration, 24.9 ml of 0.1 M HCl are added to 25.0 ml of 0.1 M NaOH. 0.2 ml more of HCl is then added. The change in pH between these two stages of titration is approximately  
a. -7.6      b. +7.0  
c. -6.6      d. +6.0
20. The acid dissociation constant, K<sub>a</sub> of H<sub>2</sub>O<sub>2</sub> is  $10^{-12}$ . The pH of a '11.2 volume' solution of H<sub>2</sub>O<sub>2</sub> is approximately  
a. 2.0      b. 3.0  
c. 4.0      d. 6.0
21. If 0.1 M solution of a weak acid is 8% ionized. Then Ka for the acid is approximately  
a.  $6.4 \times 10^{-2}$       b.  $6.4 \times 10^{-3}$   
c.  $6.4 \times 10^{-4}$       d.  $6.4 \times 10^{-6}$
22. Ka for a weak acid is  $4.0 \times 10^{-5}$ . pH of 0.001 M of the same acid is  
a. 4.3      b. 3.7  
c. 2.7      d. 3.5
23. pKa of acetic acid is 4.7. If 60 mL of 0.02 M acetic acid is mixed with 60 mL of 0.01 M NaOH, the pH of the solution is  
a. 2.7      b. 4.7  
c. 6.7      d. 8.7
24. In a 0.1 N solution of acetic acid the degree of ionization is 0.015. The OH<sup>-</sup> ion concentration is  
a.  $6.66 \times 10^{-12}$       b.  $0.666 \times 10^{-12}$   
c.  $66.6 \times 10^{-12}$       d.  $0.06 \times 10^{-12}$
25. One litre of water contains  $10^{-7}$  moles of H<sup>+</sup> ions. The percentage degree of ionization of water is  
a.  $1.6 \times 10^{-7}$       b.  $1.8 \times 10^{-7}$   
c.  $3.6 \times 10^{-7}$       d.  $36 \times 10^{-9}$

26. pH of  $\text{Ba}(\text{OH})_2$  is 12. Its solubility product is  
 a.  $5 \times 10^{-7}$       b.  $0.5 \times 10^{-7}$   
 c.  $5 \times 10^{-6}$       d.  $4 \times 10^{-6}$
27. pH of 0.01 M  $(\text{NH}_4)_2\text{SO}_4$  and 0.02 M  $\text{NH}_4\text{OH}$  buffer [ $\text{pK}_a(\text{NH}_4^+) = 9.26$ ] is  
 a.  $9.26 + \log 2$       b.  $9.26$   
 c.  $4.74 + \log 2$       d.  $4.74$
28. The solubility product of  $\text{A}_2\text{X}_3$  is  $1.08 \times 10^{-23}$ . Its solubility will be  
 a.  $1.0 \times 10^{-3}$  M      b.  $1.0 \times 10^{-4}$  M  
 c.  $1.0 \times 10^{-5}$  M      d.  $1.0 \times 10^{-6}$  M
29.  $\text{M}(\text{OH})_x$  has  $K_{\text{sp}} = 4 \times 10^{-12}$  and solubility  $10^{-4}$  M, x is  
 a. 1      b. 2  
 c. 3      d. 4
30. The number of  $\text{H}^+$  ions present in  $1 \text{ cm}^3$  of a solution whose pH is 10 is  
 a.  $10^{-10}$       b.  $10^{-13}$   
 c.  $6.02 \times 10^{10}$       d.  $6.02 \times 10^{13}$
31. What is the pH value at which  $\text{Mg}(\text{OH})_2$  begins to precipitate from a solution containing 0.10 M  $\text{Mg}^{+2}$  ion?  $K_{\text{sp}}$  of  $\text{Mg}(\text{OH})_2$  is  $1 \times 10^{-11}$ .  
 a. 3      b. 6  
 c. 9      d. 11
32. For preparing a buffer solution of pH 6 by mixing sodium acetate and acetic acid, the ratio of the concentration of salt and acid should be  
 $(\text{Ka} = 10^{-5})$   
 a. 1 : 10      b. 10 : 1  
 c. 100 : 1      d. 1 : 100
33. 50 litres of 0.1 M HCl are mixed with 50 litres of 0.2 M NaOH. The pOH of the resulting solution is
34. The pH of 0.05 M aqueous solution of diethylamine is 12. Its  $K_b$  is  
 a.  $2 \times 10^{-3}$       b.  $2.5 \times 10^{-3}$   
 c.  $3 \times 10^{-3}$       d.  $4.5 \times 10^{-3}$
35. The degree of ionization of water was found to be  $1.8 \times 10^{-9}$ . The  $K_a$  (ionization constant) of water is  
 a.  $1.8 \times 10^{-9}$       b.  $1.8 \times 10^{-16}$   
 c.  $1.0 \times 10^{-14}$       d. cannot be calculated.
36. In the titration of 50.00 mL of 0.250 M  $\text{NH}_3$  ( $K_b = 1.8 \times 10^{-5}$ ) with 0.500 M HCl, what is the equivalence point pH? (Note : remember to account for dilution.)  
 a. 2.5      b. 5.02  
 c. 6.69      d. 7.87
37. The solubility product of  $\text{P}_2\text{Q}_3$  is  $1.08 \times 10^{-23}$ . Its solubility will be  
 a.  $1.0 \times 10^{-3}$  M      b.  $1.0 \times 10^{-8}$  M  
 c.  $1.0 \times 10^{-5}$  M      d.  $1.0 \times 10^{-6}$  M
38. The number of  $\text{OH}^-$  ions in 1 mL of solution and having present pH value 4  
 a.  $6.02 \times 10^8$       b.  $6.02 \times 10^{23}$   
 c.  $6.02 \times 10^{10}$       d.  $6.02 \times 10^{13}$
39. The solubility (in mole/litre) of AgCl in 0.1 M KCl solution is (Given  $K_{\text{sp}}$  of AgCl =  $1.6 \times 10^{-10}$ )  
 a.  $1.6 \times 10^{-9}$       b.  $1.6 \times 10^{-5}$   
 c.  $1.32 \times 10^{-5}$       d.  $1.6 \times 10^{-10}$
40. What is the pH of a solution composed of 0.20 M  $\text{NH}_3$  and 0.15 M  $\text{NH}_4\text{Cl}$ ?  $K_b$  for  $\text{NH}_3$  is  $1.8 \times 10^{-5}$ .  
 a. 2.15      b. 4.62  
 c. 8.26      d. 9.38

**ANSWER KEYS**

Q.	Ans.								
1.	b	2.	d	3.	c	4.	a	5.	b
6.	c	7.	b	8.	b	9.	b	10.	c
11.	d	12.	b	13.	a	14.	b	15.	d
16.	b	17.	d	18.	d	19.	c	20.	d
21.	c	22.	b	23.	b	24.	a	25.	b
26.	a	27.	b	28.	c	29.	b	30.	c
31.	c	32.	b	33.	a	34.	b	35.	b
36.	d	37.	c	38.	d	39.	a	40.	d

## Hints and Explanations

3.  $K_f = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+] [\text{NH}_3]^2}$

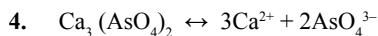
Initial conc.  $[\text{Ag}^+] = 1 \times 10^{-3} \text{ M}$

$$[\text{NH}_3] = 0.1 \text{ M}$$

$K_f$  has a high value and  $[\text{NH}_3]$  is in excess and so the  $[\text{Ag}(\text{NH}_3)_2]^+$  may be taken as equal to  $1 \times 10^{-3}$ .

$$1 \times 10^8 = \frac{1 \times 10^{-3}}{X(0.1)^2}$$

$$X = 1 \times 10^{-9} \text{ M} = [\text{Ag}^+]_{\text{eq}}$$



$$[\text{Ca}^{2+}] = 3s$$

$$[\text{AsO}_4^{3-}] = 2s$$

If the solubility is s moles lit<sup>-1</sup>, then

$$K_{sp} = [3s]^3 [2s]^2 = 108 s^5$$

$$= 108 \times (9.0 \times 10^{-5})^5$$

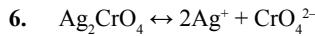
$$= 6.37 \times 10^{-19}$$

$$= 6.4 \times 10^{-19}$$

5.  $K_{sp1} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}]$

$$K_{sp2} = [\text{Ba}^{2+}] [\text{CO}_3^{2-}]$$

$$\frac{K_{sp1}}{K_{sp2}} = \frac{[\text{SO}_4^{2-}]}{[\text{CO}_3^{2-}]} = \frac{1 \times 10^{-10}}{5 \times 10^{-9}} = 0.02$$



$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = 1.686 \times 10^{-12}$$

$$= [\text{Ag}^+]^2 \times 0.02$$

$$[\text{Ag}^+] = 9.1 \times 10^{-6} \text{ M}$$

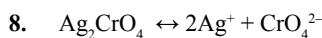
7.  $pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$

$$\log \frac{[\text{acid}]}{[\text{salt}]} = pK_a - pH$$

$$= -\log (6.4 \times 10^{-5}) - 4.5$$

$$= -0.3$$

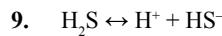
$$[\text{acid}] / [\text{salt}] = 0.5$$



$$K_{sp} = (2 \times 2 \times 10^{-4})^2 (2 \times 10^{-4})$$

$$= 32 \times 10^{-12}$$

$$= 3.2 \times 10^{-11}$$



The second dissociation constant is small and can be neglected for approximate calculation of  $[\text{H}^+]$ .

$$\text{So } 1.0 \times 10^{-7} = \frac{[\text{H}^+] [\text{HS}^-]}{0.1} = \frac{[\text{H}^+]^2}{0.1}$$

$$[\text{H}^+] = 1.0 \times 10^{-4} \text{ M}$$

$$\text{pH} = 4.0$$



So 25 ml of 0.05 M  $\text{H}_2\text{SO}_4$  requires 25.0 ml of 0.10 M NaOH solution.

$$\text{pH} = 10.6$$

$$-\log [\text{H}^+] = 10.6$$

$$\log [\text{H}^+] = -10.6 = 11.4$$

$$\text{Taking antilog, } [\text{H}^+] = 2.5 \times 10^{-11} \text{ M}$$

$$\text{So } [\text{OH}^-] = \frac{10^{-14}}{2.5 \times 10^{-11}} = \frac{1}{2.5} \times 10^{-3} \text{ M}$$

Taking the total volume as 50 ml,

number of moles of NaOH required for 50 ml

$$= \frac{1}{2.5} \times 10^{-3} \times \frac{50}{1000} .$$

For 0.10 M NaOH solution

$$0.1 \times \frac{V}{1000} = \frac{1}{2.5} \times 10^{-3} \times \frac{50}{1000} .$$

$$V = \frac{50 \times 10^{-3}}{2.5 \times 0.1} = 0.2 \text{ ml}$$

Volume of NaOH to be added = 25 + 0.2

$$= 25.2 \text{ ml}$$

11. For the salt of a weak acid and weak base

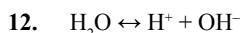
$$K_h = \frac{K_w}{K_a K_b} = \frac{h^2}{(1-h)^2} .$$

$$h / 1 - h = \sqrt{(K_w / K_a K_b)}$$

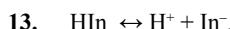
$$= (10^{-14} / 1.75 \times 4.0 \times 10^{-15})^{1/2}$$

$$= 1.195$$

$$\text{So } h = \frac{1.195}{2.195} = 0.5444$$



$$\text{K}_a = \frac{[\text{H}^+] [\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{10^{-14}}{55.5} \\ = 1.8 \times 10^{-16} \text{ mol lit}^{-1}$$

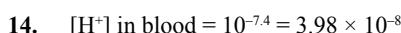


$$\text{pH} = \text{pK}_{\text{In}} + \log \frac{[\text{In}^-]}{[\text{HIn}]} = 5.5 + \log \frac{[\text{In}^-]}{[\text{HIn}]} .$$

The required upper limit of  $\text{pH} = 5.5 + \log_{10} = 6.5$ .

The required lower limit =  $5.5 + \log 0.1 = 4.5$ .

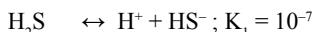
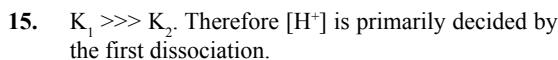
The minimum pH range is therefore 4.5 to 6.5.



$$\frac{[\text{H}^+] [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.2 \times 10^{-7};$$

$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{4.2 \times 10^{-7}}{[\text{H}^+]}$$

$$= \frac{4.2 \times 10^{-7}}{3.98 \times 10^{-8}} = 10.55 = 10.6$$



Conc:  $(0.1 - x) \quad x \quad x$

$$\frac{x^2}{0.1 - x} = 10^{-7}; \frac{x^2}{0.1} = 10^{-7}$$

$$x^2 = 10^{-8}; x = 10^{-4}$$

$$[\text{H}^+] = 10^{-4}$$

so  $\text{pH} = 4.0$



$$c(1 - \alpha) \quad \alpha c \quad \alpha c$$

$$K_1 = 4 \times 10^{-6} \approx \alpha_1^2 c$$

$$\alpha_1^2 = \frac{4 \times 10^{-6}}{c}$$

$$\alpha_1 = \frac{2 \times 10^{-3}}{c^{1/2}}$$

$$[\text{H}^+]_1 = \alpha_1 c = 2 \times 10^{-3} \times c^{1/2}$$

Similarly, for the acid HB,

$$[\text{H}^+]_{\text{II}} = \alpha_{\text{II}} c = 1 \times 10^{-4} \times c^{1/2},$$

the concentrations of HA and HB, being the same (equal to  $c$ ).

$$\frac{[\text{H}^+]_1}{[\text{H}^+]_{\text{II}}} = \frac{2 \times 10^{-3} \times c^{1/2}}{1 \times 10^{-4} \times c^{1/2}} = 20$$

19. I stage of titration: excess concentration of NaOH  $\approx 0.1 \text{ ml of } 0.1 \text{ M NaOH dilute to } 50 \text{ ml}$

$$= 0.1 \times \frac{0.1}{50} \text{ M} = 2 \times 10^{-4} \text{ M}$$

$$[\text{OH}^-] = 2 \times 10^{-4}$$

$$\text{pOH} = 4 - 0.3010 = 3.6990$$

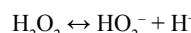
$$\text{pH} = 14 - 3.6990 = 10.3010$$

II stage of titration : excess concentration of HCl  $\approx 2 \times 10^{-4} \text{ M}$

$$\text{pH} = 3.6990$$

$$\Delta \text{pH} = 3.6990 - 10.3010 = -6.6020 = -6.6$$

20. 11.2 volume  $\text{H}_2\text{O}_2$  solution is 1 M.



$$\text{K}_a \approx \alpha^2 c = \alpha^2 \times 1 = 10^{-12}$$

$$\alpha = 10^{-6}$$

$$[\text{H}^+] = \alpha c = 10^{-6} \times 1 = 10^{-6}$$

$$\text{pH} = 6.0$$

21. For a weak acid

$$\text{Ka} = C \times \alpha^2$$

$$\alpha = 8 / 100 = 0.08$$

$$\text{Ka} = 0.1 \times 0.08 \times 0.08$$

$$= 6.4 \times 10^{-4}$$

22.  $[\text{H}_3\text{O}^+] = C \times \alpha$

$$\text{Ka} = C \times \alpha^2$$

$$\alpha = \sqrt{(\text{Ka} / C)} = \sqrt{(4.0 \times 10^{-5}) / 0.001} = 0.2$$

$$[\text{H}_3\text{O}^+] = 0.001 \times 0.2 = 0.0002$$

$$\text{pH} = -\log (0.0002) = 3.7$$

23. 60 ml of 0.01 M NaOH neutralizes 60 ml of 0.01 M acetic acid

$\text{CH}_3\text{COOH}$  in the solution

$$= \frac{60 \times 0.01}{120} = 0.005 \text{ M}$$

$$\text{pH} = \text{pKa} + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]} .$$

$$[\text{CH}_3\text{COONa}] = \frac{0.01}{2} = 0.005$$

$$= 4.7 + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]} .$$

$$= 4.7 + \log_{10} \frac{0.005}{0.005} = 4.7$$

## 5.114 ■ Ionic Equilibrium

24.  $[H^+]$  ion concentration =  $0.1 \times 0.015$   
 $= 1.5 \times 10^{-3}$  g ion / litre

$$[OH^-] = \frac{1 \times 10^{-14}}{1.5 \times 10^{-3}} = 0.666 \times 10^{-11}$$
 $= 6.66 \times 10^{-12}$

25. One litre of water  $\equiv$  1000 g of water  
 $\equiv \frac{1000}{18} = 55.5$  moles  
 55.5 moles of  $H_2O$  contains  $10^{-7}$  moles of  $H^+$  ions  
 $100$  moles of  $H_2O$  contains  $= \frac{10^{-7} \times 100}{55.5}$   
 $= 1.8 \times 10^{-7}$  moles of  $H^+$  ions

26.  $A_2X_3 \leftrightarrow 2A^{+3} + 3X^{-2}$

2S	3S
----	----

 $K_{sp} = [A^{+3}]^2 [X^{-2}]^3$ 
 $= (2S)^2 (3S)^3 = 108 S^5$ 
 $S = \left(\frac{K_{sp}}{108}\right)^{1/5} = \left(\frac{1.08 \times 10^{-23}}{180}\right)^{1/5}$ 
 $S = [10^{-25}]^{1/5} = 10^{-5}$

29.  $M(OH)x \leftrightarrow M^{+x} + x OH^-$

$10^{-4}$	$10^{-4}$	$x \times 10^{-4}$
-----------	-----------	--------------------

 $K_{sp} = [M^{+x}] [OH^-]^x = 4 \times 10^{-12}$ 
 $[10^{-4}] [x \times 10^{-4}]^x = 4 \times 10^{-12}$ 
 $[x \times 10^{-4}]^x = 4 \times 10^{-8}$ 

it holds good if  $x = 2$

30. pH = 10 means

 $[H^+] = 10^{-10} \text{ mol L}^{-1} = 10^{-13} \text{ g ions/cc}$ 
 $= 10^{-13} \times (6.02 \times 10^{23}) \text{ ions/cc}$ 
 $= 6.02 \times 10^{10} \text{ ions/cc}$

31. When  $Mg(OH)_2$  starts undergoing precipitation, then

 $[Mg^{+2}] [OH^-]^2 = K_{sp} \text{ of } Mg(OH)_2$ 
 $[0.1] [OH^-]^2 = 1 \times 10^{-11}$

$[OH^-] = 10^{-5} \text{ M}$

$\text{now } pOH = -\log [OH^-] = -\log 10^{-5} = 5$

$pH = 14 - pOH = 14 - 5 = 9$

32.  $pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

$\log \frac{[\text{Salt}]}{[\text{Acid}]} = pH - pK_a = 6 - 5 = 1$ 
 $[pK_a = -\log K_a = -\log 10^{-5} = 5]$

$\frac{[\text{Salt}]}{[\text{Acid}]} = \text{antilog}(1) = 10$

33.  $M(H^+) = \frac{M_1 V_1 (\text{base}) - M_2 V_2 (\text{acid})}{V_1 + V_2}$

 $= \frac{0.2 \times 50 - 0.1 \times 50}{100} = 5 \times 10^{-2}$

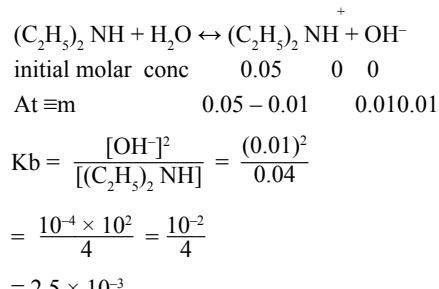
$pH = -\log [H^+] = -\log (5 \times 10^{-2})$ 
 $= 1.301$

$\text{Now, } pH + pOH = 14$

$pOH = 14 - pH$ 
 $= 14 - 1.301$ 
 $= 12.69$

34. pH = 12  $[H^+] = 10^{-12}$

$\text{Now } [OH^-] = \frac{10^{-14}}{[H^+]} = \frac{10^{-14}}{10^{-12}} = 10^{-2} \text{ M}$ 
 $= 0.01 \text{ M}$



35.  $H_2O \leftrightarrow H^+ + OH^-$

$C = \frac{1000}{18} = 55.55 \text{ M}$

$K_a = \frac{[H^+] [OH^-]}{[H_2O]} = \frac{Ca \cdot Ca}{C}$ 
 $= Ca^2$

$K_a = 55.55 \times (1.8 \times 10^{-9})^2$ 
 $= 1.8 \times 10^{-16}$

37.  $P_2Q_3 \equiv 2P^{3+} + 3Q^{2-}$

2S	3S
----	----

$$K_{sp} = [P^{3+}]^2 [Q^{2-}]^3$$

$$[2S]^2 \quad [3S]^3$$

$$= 108 S^5$$

$$S = \left( \frac{K_{sp}}{108} \right)^{1/5} = \left( \frac{1.08 \times 10^{-23}}{108} \right)^{1/5}$$

$$= [10-25]^{1/5} = 10^{-5}$$

$$S = 10^{-5} M$$

38. As pH = 4

$$H^+ = 10^{-4}$$

$$\text{Since } [H^+] [\text{OH}^-] = 10^{-14}$$

$$[\text{OH}^-] = \frac{10^{-14}}{[H^+]} = \frac{10^{-14}}{10^{-4}} = 10^{-10} \text{ g ion/litre}$$

$$[\text{OH}^-] = 6.023 \times 10^{23} \times 10^{-10}$$

$$= 6.023 \times 10^{13} \text{ ion/litre.}$$

$$= \frac{6.023 \times 10^{13} \text{ ion}}{1000 \text{ mL}}$$

$$= 6.023 \times 10^{10} \text{ ion/mL.}$$

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## CHAPTER 6

# Electrochemistry

### Chapter Contents

Electrochemical cells and cell reactions; Standard electrode potentials; Nernst equation and its relation of  $\Delta G$ ; Electrochemical series, emf of galvanic cells; Faraday's laws of electrolysis; Electrolytic conductance, specific, equivalent and molar conductivity, Kohlrausch's laws Concentration cells and Various levels of multiple-choice questions.

## ELECTROCHEMISTRY

Electrochemistry is the branch of the science that deals with the transformation of chemical energy into electrical energy and vice versa or it deals with the relationship between electrical and chemical energy produced in a redox reaction.

## ELECTROLYSIS

Here direct current is used to cause a non-spontaneous chemical reaction due to it chemical decomposition of electrolytes takes place or It is the flow of electrons across the boundary followed by a chemical reaction that is, redox reaction. It occurs in electrolytic cell and it takes place at electrodes.

- The electrode which is connected to the positive pole of the battery is known as anode or positive electrode.
- At anode, de-electronation of anions or oxidation takes place.



- The electrode which is connected to the negative pole of the battery is known as cathode or negative electrode.
- At cathode, electronation of cation or reduction takes place.
- $$B^+ + e^- \rightarrow B$$
- It is interesting to note that the current enters the electrolyte through cathode while leaves through anode.
- The electrolyte as a whole remains neutral during the process of electrolysis as equal number of charges are neutralized at the electrodes.
- Electrodes are two types: (i) Inert and (ii) Active
- If inert electrode is used, the products formed at cathode and anode depends upon nature of electrolytes.
- If active electrode is used at cathode metal deposits and at anode metal is dissolved.

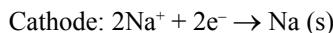
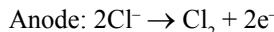
## 6.2 ■ Electrochemistry

- Example, If Ni deposits at cathode, it is called electroplating.
- When fused salts are electrolyzed by using inert electrodes they ionize into their constituent elements.
- Example,  $\text{NaCl} \rightarrow \text{Na} + \frac{1}{2} \text{Cl}_2$   
 $\text{NiCl}_2 \rightarrow \text{Ni} + \text{Cl}_2$
- When fused salts are electrolyzed by using active electrodes anode get dissolved due to formation of ions while cathode increases due to deposition of metal on it.
  - During electrolysis of aq. solution of  $\text{AgNO}_3$ , the concentration of  $\text{AgNO}_3$  is found to be same before and after electrolysis.
  - During the electrolysis of aqueous solution of salts having  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  (oxo anions) only water molecule undergo oxidation to liberate  $\text{O}_2$  at anode.
  - During electrolysis of aqueous solution of alkali or alkaline earth metals, only water molecules undergo reduction to liberate hydrogen at cathode.

Feature	Cathode	Anode
Sign	Negative as attached to negative end of external battery	Positive as attached to positive end of external battery
Direction of movement of electrons	Into the cell	Out of the cell
Direction of movement of ions	Cations	Anions
Half-reaction	Reduction	Oxidation

## Examples of Electrolysis

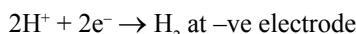
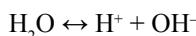
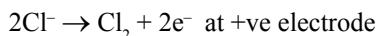
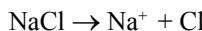
- (i) Electrolysis of Molten or Fused NaCl:



Net reaction:



- (ii) Electrolysis of Aqueous NaCl Solution



As NaOH is in solution so pH increases.

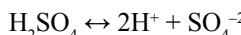
At anode,  $\text{Cl}^-$  donate  $\text{e}^-$  as  $E_{\text{O.P.}} < E_{\text{R.P.}}$  of  $\text{OH}^-$

At cathode,  $\text{H}^+$  accept  $\text{e}^-$  as  $E_{\text{R.P.}} \text{ of H}^+ > E_{\text{R.P.}}$  of  $\text{Na}^+$

$\text{O}_2$  is not formed at anode here as over voltage is very high for it.

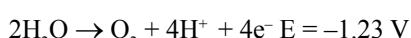
- (iii) Electrolysis of  $\text{H}_2\text{SO}_4$ :

For pure  $\text{H}_2\text{SO}_4$  electrolysis is not possible due to absence of ions.



Solution becomes colourless and pH decreases as  $\text{H}_2\text{SO}_4$  is formed.

If further electrolysis is done  $\text{O}_2$  is released at anode and  $\text{H}_2$  is released at cathode.



'g' 'aq'

## Electrolysis of some electrolytes

S. No	Electrolytes	Electrodes		Products			Electrode reactions	
		Anode	cathode	At anode	At cathode	At anode	At cathode	At cathode
1	NaCl (fused)	Pt	Pt	$\text{Cl}_2$	Na	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	
2	MgCl <sub>2</sub> (fused)	Graphite	Steel	$\text{Cl}_2$	Mg	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	

3	$\text{Al}_2\text{O}_3$ (fused + cryolite)	Graphite	Graphite	$\text{F}_2$	Al	$2\text{F}^- \rightarrow \text{F}_2 + 2\text{e}^-$	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$
4	$\text{NiCl}_2$ (fused)	Pt	Pt	$\text{Cl}_2$	Ni	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$
5	$\text{NaCl}$ (aq)	Pt	Pt	$\text{O}_2, \text{Cl}_2$	$\text{H}_2$	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$
6	$\text{AgNO}_3$ (aq)	Pt Ag	Pt Pt	$\text{O}_2$ $\text{O}_2, \text{Ag}^+$	Ag Ag	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ $\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$
7	$\text{CuSO}_4$ (aq)	Pt	Pt	$\text{O}_2$	Cu	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
8	50% $\text{H}_2\text{SO}_4$ (aq)	Pt	Pt	$\text{H}_2\text{S}_2\text{O}_8$	$\text{H}_2$	$2\text{HSO}_4^- \rightarrow \text{H}_2\text{S}_2\text{O}_8 + 2\text{e}^-$	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
9	$\text{K}_2\text{SO}_4$ (aq)	Pt	Pt	$\text{O}_2$	$\text{H}_2$	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$
10	$\text{CuCl}_2$ (mol- ten)	Pt Cu	Pt Pt	$\text{Cl}_2$ $\text{Cu}^{2+}$	Cu Cu	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$

**REMEMBER**

- The apparatus used for measurement of quantity of electricity is called Coulometer.
- The amount of ion discharged during electrolysis is independent of resistance of solution and temperature of bath.
- The art of electroplating was given by Faraday.

**Product of Electrolysis**

According to preferential discharge theory the ion will discharge first which required less energy. The potential at which ion get discharged is called deposition potential or discharge potential.

$$\text{Discharge potential} = \text{Electrode potential} + \text{Over voltage}$$

**FARADAY'S LAWS OF ELECTROLYSIS****Faraday's First Law of Electrolytes**

According to the first law, "The amount of substance or quantity of chemical reaction at electrode is directly proportional to the quantity of electricity passed into the cell".

$$W \text{ or } m \propto q$$

$$\text{or } W \propto It$$

$$W = Zit$$

$$Z = \frac{M}{nf}$$

Z = Electrochemical equivalence

M = molar mass

F = 96500

n = Number of electrons transfer

q = amount of charge utilized

## 6.4 ■ Electrochemistry

Electrochemical equivalent is the amount of the substance deposited or liberated by one ampere current passing for one second (that is, one coulomb,  $I \times t = Q$ ) or one coulomb of charge.

One gm equivalent of any substance is liberated by one faraday.

$$\text{Eq. Wt.} = Z \times 96500$$

$$\frac{W}{E} = \frac{q}{96500}$$

$$w = \frac{E \cdot q}{96500}$$

$$w = \frac{E \cdot i \cdot t}{96500}$$

As  $w = a \times l \times d$  that is, area  $\times$  length  $\times$  density

Here  $a$  = area of the object to be electroplated

$d$  = density of metal to be deposited

$l$  = thickness of layer deposited

Hence from here we can predict charge, current strength time, thickness of deposited layer etc.

### REMEMBER

**One Faraday:** One faraday is the quantity of charge carried by one mole of electrons.

$$E \propto Z$$

$$E = FZ$$

$$1 F = 1.6023 \times 10^{-19} \times 6.023 \times 10^{23}$$

$$= 96500 \text{ Coulombs}$$

## Faraday's Second Law of Electrolytes

According to the second law, "When the same quantity of electricity is passed through different electrolytes, the amounts of the products obtained at the electrodes are directly proportional to their chemical equivalents or equivalent weights".

$$\text{As } \frac{W}{E} = \frac{q}{96500} = \text{No. of equivalents constant}$$

So

$$\frac{E_1}{E_2} = \frac{M_1}{M_2} \text{ or } \frac{W_1}{W_2} = \frac{Z_1 I t}{Z_2 I t} = \frac{Z_1}{Z_2}$$

$E_1$  = equivalent weight mass

$E_2$  = equivalent weight mass

$W$  or  $M$  = mass deposited

From this law, it is clear that 96500 coulomb of electricity gives one equivalent of any substance  
Example,  $1F = 1 \text{ gm eq}$

## Application of Faraday's Laws

- It is used in electroplating of metals.
- It is used in the extraction of several metals in pure form.
- It is used in the separation of metals from non-metals.
- It is used in the preparation of compounds

### REMEMBER

## Current Efficiency

It is the ratio of the mass of the products actually liberated at the electrode to the theoretical mass that could be obtained

$$\text{C.E.} = \frac{\text{desired extent}}{\text{Theoretical extent of reaction}} \times 100\%$$

## Illustrations

1. A solution of a salt of a metal of atomic weight 112 was electrolysed for 150 minutes with a current of 0.15 amperes. The weight of metal deposited was 0.783 mg. Find the equivalent weight and valency of the metal in the salt.

**Solution** Given:  $I = 0.15 \text{ ampere}$

$$t = 150 \times 60 \text{ seconds}$$

$$Q = I \times t$$

$$Q = 0.15 \times 150 \times 60 \text{ coulombs}$$

$$= 1350 \text{ coulombs}$$

1350 coulombs of electricity deposit = 0.783 gm of metal

96540 coulombs of electricity

$$= \frac{0.783 \times 96540}{1350} \text{ gm} = 55.97 \text{ gm of metal}$$

Equivalent weight of metal = 55.97

$$\text{Valency of metal} = \frac{\text{Atomic weight}}{\text{Equivalent weight}}$$

$$= \frac{112}{55.97} = 2$$

2. A current of 3.7 amperes is passed for 360 minutes between nickel electrodes of a 2 M solution of  $\text{Ni}(\text{NO}_3)_2$ . What will be the molarity of the solution at the end of the electrolysis? (At. wt. of Ni = 58.70)

**Solution**  $\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni} (\text{s})$

$$w = \frac{E \cdot i \cdot t}{F}$$

$$= \frac{58.70 \times 3.7 \times 360 \times 60}{96500 \times 2} = 24.307 \text{ g}$$

Number of moles of Ni deposited

$$= \frac{24.307}{58.70} = 0.414 \text{ mole}$$

$$\begin{aligned} \text{Molarity of remaining solution} &= 2.0 - 0.414 \\ &= 1.586 \text{ M} \end{aligned}$$

3. How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8.0 hours at a current of 8.46 amperes? What is the area of the tray if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm<sup>3</sup>.

**Solution**  $\text{Ag}^+ + 1\text{e}^- \rightarrow \text{Ag} (\text{s})$

$$\text{Wt. of Ag} = \frac{E \cdot i \cdot t}{F}$$

$$= \frac{107.9 \times 8.46 \times 8 \times 60 \times 60}{96500} = 272.43 \text{ g}$$

$$\text{Volume of Ag} = \frac{\text{Wt. of Ag}}{\text{density}} = \frac{272.43}{10.5} = 25.94 \text{ ml}$$

$$\begin{aligned} \text{Area of tray} &= \frac{\text{Volume}}{\text{Thickness}} = \frac{25.94}{0.00254} \\ &= 10212.6 \text{ cm}^2 \end{aligned}$$

4. A copper coulometer and a silver coulometer were connected in series. The copper coulometer contained a 5% solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  while the silver coulometer contained a 2% solution of  $\text{AgNO}_3$ . A current of 0.01 ampere was passed through the coulometers for 30 minutes. What was the ratio of the masses of Cu and Ag deposited at the cathode of the two coulometers respectively?

**Solution**  $W = Z \cdot i \cdot t$

For copper

$$W = \frac{31.75}{96500} \times 0.01 \times 30 \times 60$$

$$= 0.0059 \text{ g}$$

For silver

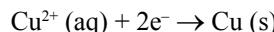
$$W = \frac{108}{96500} \times 0.01 \times 30 \times 60$$

$$= 0.0201 \text{ g}$$

Thus ratio of the masses of Cu and Ag deposited at the cathode is

$$0.0059 : 0.0201 = 1 : 3.407$$

5. When an aqueous solution of copper (II) sulphate,  $\text{CuSO}_4$  is electrolyzed copper metal is deposited



If a constant current was passed for 5.0 hour, 404 mg of copper metal was deposited, what must have been the current?

**Solution** According to Faraday's first law of electrolysis,

$$m = Z \cdot i \cdot t$$

$$404 \times 10^{-3} \text{ g} = \frac{63 \text{ g C}^{-1}}{2 \times 96500} \times i \times 5 \times 60 \times 60$$

$$i = \frac{0.404 \times 2 \times 96500}{63 \times 5 \times 60 \times 60}$$

$$= 0.0682 \text{ ampere}$$

6. How long will it take 5 amperes of current to deposit 2 g of copper from a solution of copper sulphate? (Equivalent wt. of Cu = 32, F = 96500 C)

**Solution**  $W = Z \cdot i \cdot t$

$$2 \text{ g} = \frac{32 \text{ g}}{96500 \text{ C}} \times 5 \text{ amp} \times t$$

$$t = \frac{2 \times 96500}{32 \times 5}$$

$$= 1206.25 \text{ s.}$$

## 6.6 ■ Electrochemistry

7. During the electrolysis of an aqueous solution of NaCl 10.3 g of chlorine was liberated. Calculate the volume of hydrogen that would be liberated at 20°C and 740 mm of Hg pressure from acidulated water, when the same quantity of current as that used in the electrolysis of NaCl was passed.

### Solution

According to Faraday's law of electrolysis, as the current passed will be the same

$$\frac{\text{Weight of H}_2 \text{ liberated}}{\text{Eq. weight of H}_2} = \frac{\text{Weight of Cl}_2 \text{ liberated}}{\text{Eq. weight of Cl}_2}$$

$$\frac{\text{Weight of H}_2 \text{ liberated}}{1} = \frac{10.3}{35.5}.$$

$$\text{Weight of H}_2 \text{ liberated} = \frac{10.3}{35.5} \text{ g}$$

As 2 g of H<sub>2</sub> occupies 22400 cc at NTP

$$\text{So } \frac{10.3}{35.5} \text{ g occupies } \frac{22400 \times 10.3}{2 \times 35.5} = 3249 \text{ cc}$$

The volume of H<sub>2</sub> at 20°C and 740 mm of Hg pressure will be from

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V = \frac{3249 \times 760 \times 293}{273 \times 740} = 3582 \text{ cc}$$

## ELECTRICAL CONDUCTANCE

Here, conductance is due to movement of ions through electrodes. It involves transfer of matter and ions. It occurs in small magnitude. Besides nature of material, the magnitude of conductivity also depends upon temperature and pressure at which the measurements are made.

- The conductivity of electrolytic solutions depends upon
  - (a) Nature of electrolyte
  - (b) Size of ions produced and their solvation (hydration)
  - (c) Nature of solvent and its viscosity
  - (d) Concentration of the electrolytes
  - (e) Temperature (direct relation)
- Electronic conductance through metals is known as metallic or electronic conductance and it is

due to the moment of electrons the conductivity of metals depends upon:

- (a) Nature of structure of metal
- (b) Number of valence electrons per atom
- (c) Density of metal
- (d) Temperature (inverse relation)

■ As the electrons enter at one end go out at the other end, the composition of the metallic conductor remains unchanged. In contrast to electrolytic conductance, electronic conductance decreases with increase in temperature.

## Ohm's Law

According to Ohm's law,

$$\frac{E}{I} = \text{constant (R)}$$

or

$$I = \frac{E}{R}$$

E = potential, R = resistance

Unit : Ω ohms

## Resistance (R)

It offers obstruction to the passage of electric current. It is directly proportional to the length (l) and inversely proportional to the area of cross section (a) of the conductor.

$$R \propto l/a \text{ or } R = \frac{\rho l}{a}$$

## Specific Resistance ( $\rho$ )

The resistance offered by one cm<sup>3</sup> of the conductor is known as specific resistance.

If l = 1 cm

If a = 1 cm<sup>2</sup>

$$R = \rho$$

$$\rho = R \cdot \frac{a}{l} \text{ ohm. cm.}$$

## Conductance (C)

It is ease of flow of electric current through the conductor and it is reciprocal of resistance.

$$C = \frac{1}{R} \Omega^{-} (\text{mho})$$

$$1S = 1 \Omega^{-}$$

siemens

## Specific Conductance (k, kappa)

It is the reciprocal of specific conductance.

$$k = \frac{1}{\rho} = \frac{1}{R \cdot a}$$

$\frac{1}{a}$  = cell constant

Unit:  $\Omega^{-1} \text{cm}^{-1}$

- If 'l' and 'a' are unity then conductance of one c.c. is called specific conductance or conductivity

## Cell Constant

$$\text{Cell constant} = \frac{\text{Specific conductance}}{\text{Measured conductance}}$$

Conductance is measured by using wheat stone bridge method (for R) and 1N or .01 N KCl solution for [l/a]

## Effect of Dilution on specific Conductance

The number of current carrying particles or ions per ml decrease on dilution and specific conductivity, being the conductance of one centimeter cube of solution, decreases with dilution.

## Equivalent Conductivity

The conductivity of all the ions produced when one gram equivalent of an electrolyte is dissolved in V ml of solution is called equivalent conductivity. It is denoted by  $\lambda_v$  or  $\Lambda_v$ .

$$\lambda \text{ or } \Lambda = k \times V.$$

Unit:  $\Omega^{-1} \text{c. m}^2$

$$\text{As } \frac{W}{E} = \frac{NV}{1000}$$

$$\text{So } \lambda = \frac{k \times 1000}{N}$$

- The equivalent conductivity increases with increase of dilution.

## Molar Conductivity

The conductivity of all the ions produced when one mole of an electrolyte is dissolved in V ml of solution is known as molar conductivity.

$$\lambda_m \text{ or } \Lambda_m = \frac{1000 \times k \times V}{M \text{ (molarity)}}$$

## Factors Affecting the Molar Conductivity ( $\Lambda_m$ )

- Nature of Electrolyte:** Strong electrolytes like HCl,  $\text{H}_2\text{SO}_4$ , NaOH, KOH,  $\text{KNO}_3$ , KCl,  $\text{NH}_4\text{NO}_3$  etc., are completely ionized in aqueous solution so have high value of molar conductivity.

As weak electrolytes like  $\text{H}_2\text{CO}_3$ ,  $\text{CH}_2\text{COOH}$ ,  $\text{NH}_4\text{OH}$  etc., are ionized to lesser extent in aqueous solution so have lower value of molar conductivity.

### Temperature

$$\Lambda_m \propto \text{Temperature}$$

As the increase of temperature decreases inter ionic attractions, solvation of ions, viscosity and increases kinetic energy of ions and their speed so  $\Lambda_m$  increases with the increase of temperature.

- Dielectric Constant of Solvent:** Higher the value of dielectric constant of a solvent, the more is the value of molar conductivity as it decreases inter ionic attractions.

$$\blacksquare K = \frac{C \cdot (\Lambda^\circ / \Lambda_m)_2}{1 - \Lambda^\circ / \Lambda_m}.$$

### Viscosity of Solvent

$$\Lambda_m \propto 1/\eta$$

that is, higher the value of viscosity lower is the value of molar conductivity.

## Effect of Dilution on Molar Conductivity

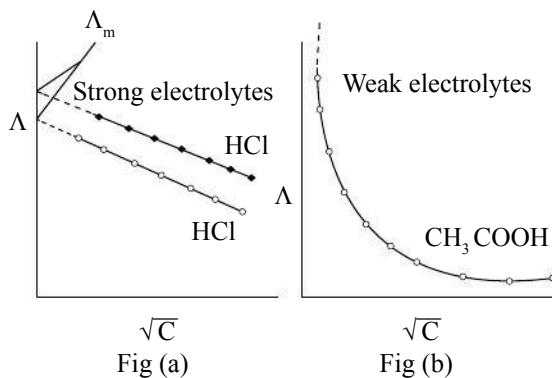
Molar conductivity increases with dilution as degree of dissociation of electrolyte increase with dilution. At  $\infty$  Dilution  $\Lambda$  is maximum i.e.,  $\Lambda_\infty$  is maximum.

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty}$$

### Concentration of the Solution

As the concentrated solutions of strong electrolytes have significant inter ionic attractions, which reduces the speed of ions so lowers the value of molar conductivity. As the dilution decreases such attractions so increases the value of molar conductivity.

The limiting value of  $\Lambda_m$  ( $\Lambda_m^\infty$  the molar conductivity at zero concentration or at infinite dilution) can be obtained by extrapolating the graph shown below.



Variation of molar conductance ( $\Lambda$ ) with square root of concentration  $\sqrt{C}$  (a) Strong electrolytes and (b) Weak electrolytes

The variation in molar conductance with concentration is different for strong and weak electrolytes.

### Debye–Hückel–Onsager Equation

It shows a relation between molar conductivity at a particular concentration and molar concentration at infinite dilution as follows:

$$\Delta m = \Lambda_m^\infty - b\sqrt{C}$$

or

$$\mu = \mu_\infty - b\sqrt{C}$$

Here,  $b$  = Constant,

$C$  = Concentration;

$\Lambda_m^\infty$  or  $\mu_\infty$  = Molar conductance at infinity.

$\Lambda_m$  or  $\mu$  = Molar conductance at other dilutions  
The value of  $b$  for a given solvent and temperature depends upon the nature of electrolyte that is, the charges on cation and anion produced after dissociation (thus NaCl, CaCl<sub>2</sub>, MgSO<sub>4</sub> are known as 1–1, 2–1 and 2–2 electrolytes respectively). All electrolytes of a particular type have same value of  $b$ . The value of  $b$  is obtained from the slope value.

### Kohlrausch Law

Kohlrausch examined  $\Lambda^\circ$  or  $\Lambda^\infty$  values for a number of strong electrolytes and observed certain regularities. He noted that the difference in  $\Lambda^\circ$  of the electrolytes NaX and KX for any X in nearly constant.

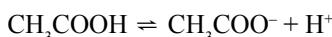
On the basis of these observations he introduced **Kohlrausch law of Independent Migration of ions**. The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the

electrolyte, that is, at infinite dilution, the contribution of any ion towards equivalent conductance is constant; it does not depend upon presence of any ion.

For any electrolyte:



$$\Lambda^\circ = X \lambda_{+}^\circ + Y \lambda_{-}^\circ$$



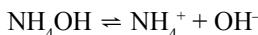
$$\begin{aligned}\Lambda_m^\infty (CH_3COOH) &= (\Lambda_H^\infty + \Lambda_{Cl}^\infty) + (\Lambda_{CH_3COO^-}^\infty + \Lambda_{Na^+}^\infty) \\ &\quad - (\Lambda_{Na^+}^\infty - \Lambda_{Cl^-}^\infty) \\ &= \Lambda_{HCl}^\infty + \Lambda_{CH_3COONa}^\infty - \Lambda_{NaCl}^\infty\end{aligned}$$

### Application of Kohlrausch's Law

#### 1. Determination of $\Lambda^\circ B$ of a weak electrolyte:

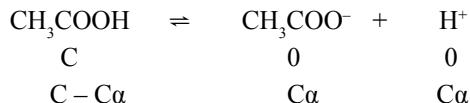
In case of weak electrolytes, the degree of ionization increases which increases the value of  $\Lambda_m$ . However, it cannot be obtained by extrapolating the graph. The limiting value,  $\Lambda_m^\infty$ , for weak electrolytes can be obtained by Kohlrausch law.

for example in case of NH<sub>4</sub>OH



$$\begin{aligned}\Lambda_m^\infty (NH_4OH) &= (\Lambda_{NH_4}^\infty + \Lambda_{Cl}^\infty) + (\Lambda_{Na^+}^\infty + \Lambda_{OH^-}^\infty) \\ &\quad - (\Lambda_{Na^+}^\infty - \Lambda_{Cl}^\infty) \\ &= \Lambda_{NH_4Cl}^\infty + \Lambda_{NaOH}^\infty - \Lambda_{NaCl}^\infty\end{aligned}$$

#### 2. To determine degree of dissociation and equilibrium constant of weak electrolyte:



Here  $C$  = Initial concentration

$\alpha$  = Degree of dissociation

$$\alpha = \frac{\Lambda^\circ}{\Lambda_m} .$$

Here  $\Lambda^\circ$  or  $\Lambda^\infty$  = Molar conductance at infinite dilution or zero concentration.

$\Lambda_m$  = Molar conductance at given conc.  $C$

$$K = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$K = \frac{C\alpha \cdot C\alpha}{C(1 - \alpha)}$$

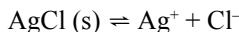
$$K = \frac{Ca^2}{1 - \alpha}.$$

$$K = \frac{C \cdot (\Lambda^\circ / \Lambda_M)^2}{(1 - \Lambda^\circ / \Lambda_M)}.$$

$$= \frac{C (\Lambda^\circ)^2}{\Lambda^\circ (\Lambda^\circ - \Lambda_m)}$$

These are Ostwald's relations.

3. To determine solubility of salt and  $K_{sp}$ :



$$\Lambda^\circ = \frac{1000 \text{ K}}{\text{M}}$$

$$\Lambda^\circ = \lambda^\circ \text{Ag}^+ + \lambda^\circ \text{Cl}^-$$

$$\text{M} = \frac{1000 \text{ K}}{\Lambda^\circ}$$

Here M = Solubility of AgCl

Solubility product:

$$K_{sp} = [\text{Ag}^+] [\text{Cl}^-]$$

$$\text{As } [\text{Ag}^+] = [\text{Cl}^-]$$

$$K_{sp} = \frac{1000 \text{ K}}{\Lambda^\circ} \times \frac{1000 \text{ K}}{\Lambda^\circ}$$

$$K_{sp} = (1000 \text{ K}/\Lambda^\circ)^2$$

## Illustrations

8. Calculate the equivalent conductivity of 1M  $\text{H}_2\text{SO}_4$  solution, if its conductivity is  $26 \times 10^{-2}$  ohm $^{-1}$  cm $^{-1}$ . (Atomic weight of sulphur = 32)

**Solution**  $N = nM = 2 \times 1 \text{ M} = 2N$

As  $\text{H}_2\text{SO}_4$  is a diprotic acid so  $n = 2$

$k$  = Specific conductivity =  $26 \times 10^{-2}$  ohm $^{-1}$  cm $^{-1}$

$$\Lambda_{eq} = \frac{1000 k}{N} = \text{ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

$$= \frac{1000 \times 26 \times 10^{-2}}{2N}$$

$$= 1.3 \times 10^2 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

9. If  $\Lambda_m^\circ$  of HCl, NaCl and  $\text{CH}_3\text{COONa}$  are 425, 128 and  $96 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  respectively, calculate the value of  $\Lambda_m^\circ$  for acetic acid.

$$\begin{aligned} \text{Solution } \Lambda_m^\circ \text{ CH}_3\text{COOH} &= \Lambda_m^\circ \text{ CH}_3\text{COOH} + \Lambda_m^\circ \text{ HCl} \\ &\quad - \Lambda_m^\circ \text{ NaCl} \\ &= 96.0 + 425.0 - 128.0 \\ &= 393.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \end{aligned}$$

10. A salt solution of 0.30 N placed in a cell whose electrodes are 1.9 cm apart and  $3.6 \text{ cm}^2$  in area offers a resistance pf  $20 \Omega$ . Calculate equivalent conductivity of solution.

**Solution**  $R = 20 \Omega, l = 1.9 \text{ cm}$

$$a = 3.6 \text{ cm}^2, N = 0.30 \text{ N}$$

$$\text{Cell constant} = \frac{1}{a} = \frac{1.9}{3.6} = 0.528 \text{ cm}^{-1}$$

Specific conductance (k) = conductance  $\times$  cell constant =  $(1/R) \times$  cell constant

$$= (1/20) \times 0.528$$

$$= 0.0264 \text{ s cm}^{-1}$$

$$\Lambda_{eq} = \frac{k \times 1000}{N} = \frac{0.0264 \times 1000}{0.30}$$

$$= 88 \text{ s cm}^2 \text{ eq}^{-1}.$$

11. 0.05 M NaOH solution offered a resistance of  $31.16 \Omega$  in a conductivity cell at 298 K. If cell constant is  $0.367 \text{ cm}^{-1}$ . Find out the molar conductivity of NaOH solution.

**Solution** Conductivity (k) =  $\frac{\text{Cell constant}}{R}$

$$= \frac{0.367}{31.16} = 0.0118 \text{ s cm}^{-1}$$

$$\Lambda_m = \frac{k \times 1000}{M} = \frac{0.0118 \times 1000}{0.05}$$

$$= 236 \text{ s cm}^2 \text{ mol}^{-1}$$

12. The molar conductivities of  $\text{CH}_3\text{COOH}$  at 25°C at the concentration of 0.1 M and 0.001 M are 5.20 and  $49.2 \text{ s cm}^2 \text{ mol}^{-1}$  respectively. Calculate the degree of dissociation of  $\text{CH}_3\text{COOH}$  at these concentrations. ( $\Lambda_m^\circ (\text{CH}_3\text{COOH}) = 390.7 \text{ s cm}^2 \text{ mol}^{-1}$ )

**Solution** Degree of dissociation ( $\alpha$ ) =  $\frac{\Lambda_m^\circ}{\Lambda_m^\circ}$

## 6.10 ■ Electrochemistry

$$= \frac{5.20}{390.7} = 0.013 = 1.3\%$$

$$0.001 \text{ M} = \frac{49.2}{390.7} = 0.125 = 12.5\%$$

### Electrochemical Cell or Galvanic Cell or Voltaic Cell

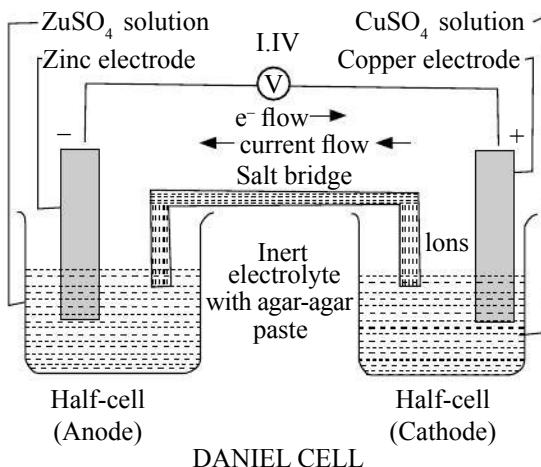
It is the device in which the decrease of free energy during the indirect redox reaction is made to convert chemical energy into electrical energy.

Galvanic and Voltaic developed such devices therefore these cells are also known as Galvanic cells or Voltaic cell or Redox cells.

Feature	Cathode	Anode
Sign	Positive due to consumption of electrons	Negative due to release of electrons
Reaction	Reduction	Oxidation
Movement of electrons	Into the cell	Out of cell

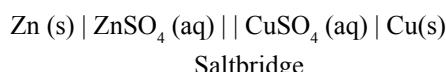
Electrochemical Cell	Electrolytic Cell
It is a combination of two half cells, containing the same or different electrodes in the same or different electrolytes.	It is a single cell containing the same electrodes present in the same electrolyte.
Anode is negative, cathode is positive Electrons move from anode to cathode in external circuit	Anode is positive, cathode is negative Electrons enter through cathode and leave through anode.
It converts chemical energy into electrical energy, produced as a result of redox reaction.	It converts electrical energy into chemical energy. Energy is supplied to the electrolytic solution to bring about the redox reaction.
Cell reaction is spontaneous.	Cell reaction is non spontaneous.
Salt bridge is required.	No salt bridge is required.

### Galvanic or Daniel cell

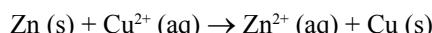


■ The Daniel cell is a typical galvanic cell. It is designed to make use of the spontaneous redox reaction between zinc and cupric ion to produce an electric current.

■ The Daniel cell can be conventionally represented as



■ The Daniel cell reaction is represented as



■ In Daniel cell, electrons flow from zinc electrode to copper electrode through external circuit while metal ions flow from one half cell to the other through salt bridge.

■ Here current flows from copper electrode to zinc electrode that is, cathode to anode in external circuit.

■ Daniel cell is a reversible cell while a voltaic cell may be reversible or irreversible.

A voltaic cell is reversible only when it satisfies following conditions:

■ The emf of external source is more than that of voltaic cell so that current may flow from external source into the voltaic cell and cell reaction can be reversed.

■ If emf of voltaic cell is more than that of external source current flows from voltaic cell into external source.

## Saltbridge

It maintains electrical neutrality in two compartments by allowing movement of anions towards anodic compartment and cations towards cathodic compartment.

- It is a glass tube having KCl,  $\text{KNO}_3$ , ammonium nitrate in a gelatin gel or agar–agar past.
- The gelatin gel allows ionic movement through it but prevents any kind of mixing.
- In case of KCl or ammonium nitrate, the ionic mobility of cation and anion are same.

## Function of a Saltbridge

- A salt bridge acts as an electrical contact between the two half-cells.
- It prevents mechanical flow of solution but it provides free path for the migration of ions to maintain an electric current through the electrolyte solution. It prevents the accumulation of charges.
- A salt bridge helps in maintaining the charge balance in the two half cells.
- A salt bridge minimizes/eliminates the liquid junction potential.

**Liquid Junction Potential:** The unequal rates of migration of the cations and anions across a liquid–liquid junction give rise to a potential difference across the junction. This potential difference across the liquid–liquid junction is called liquid junction potential.

### REMEMBER

- If salt bridge is removed the emf of the cell drops to zero.

## Electrodes or Half Cells

- An electrode and the solution in which it is dipped is called a half-cell.
- Half cells are called anodic half cells and cathodic half cells.
- The electrode at which oxidation takes place is called anode.
- The electrode at which reduction takes place is called cathode.

- Anode is positively charged and cathode is negatively charged in electrolytic cell.
- In voltaic cell anode has negative charge as the electron will flow from it.
- In voltaic cell cathode has positive charge as the electrons are drawn from it.
- At anode deelectronation or oxidation occurs as the elements goes into the solution due to loss of electrons by ions.
- At cathode electronation or reduction process occurs as ions gain electron and get discharged here.

## Types of Electrodes or Half Cells

The various types of electrodes which are frequently used in the electrochemical cells are as follows:

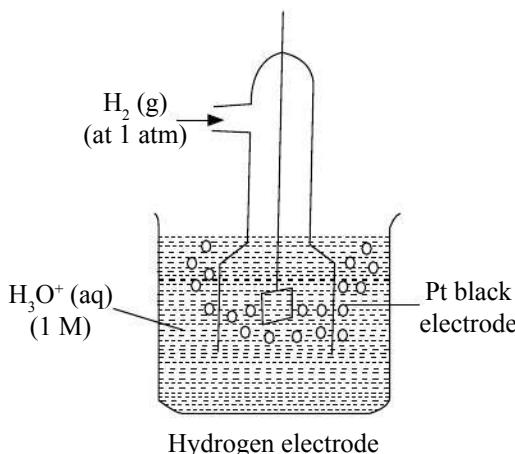
1. **Metal-Metal Ion Electrode:** It includes a metal strip dipped in the solution of its own cations.  
Example,  $\text{Zn}/\text{Zn}^{2+}$ ,  $\text{Cu}/\text{Cu}^{2+}$ ,  $\text{Ag}/\text{Ag}^+$  etc.
2. **Amalgam Electrode:** It is similar to metal–metal ion type electrode, but here, metal is replaced by its amalgam with Hg. This is done to improve the activity of metal.  
Example,  $\text{Zn} - \text{Hg}/\text{Zn}^{2+}$
3. **Gas Electrode:** It involves the inert metal foil like Pt immersed in the solution capable of furnishing ions of gas.  
Example, Pt,  $\text{H}_2/\text{H}^+$  and Pt,  $\text{Cl}_2/\text{Cl}^-$
4. **Metal-Metal Insoluble Salt-Salt Anion:** This type of electrode includes metal in contact with its sparingly soluble salt and aqueous solution of solution salt containing same anion.  
Example,  $\text{Hg} - \text{Hg}_2\text{Cl}_2(s) - \text{KCl(aq)}$  Calomel electrode  
 $\text{Pb} - \text{PbSO}_4(s) - \text{K}_2\text{SO}_4(aq)$
5. **Redox Electrode:** This electrode includes a platinum wire dipped in a solution of mixture of the two salts of the same metal but with different oxidation states.  
Example, Pt,  $\text{Fe}^{2+}/\text{Fe}^{3+}$ .
6. **Glass Electrode:**  
It consists of a thin walled glass bulb made out of special types of low melting glass.  
Glass electrodes are not affected by oxidizing and reducing agents and are not easily poisoned so

## 6.12 ■ Electrochemistry

they are finding great applications, in industry, in analytical chemical and biological laboratories in the measurement of pH.

Glass electrode gives very good results for pH value ranging between 0 and 6. For solutions of high alkalinity, high accuracy is not obtained.

### 7. Standard Hydrogen Electrode (SHE):



A hydrogen electrode in which pressure of hydrogen gas is maintained at 1 atm and the concentration of H<sup>+</sup> ions in the solution is 1 M, is called a standard hydrogen electrode (SHE).

SHE half reaction      Electrode potential



- The emf of a standard hydrogen electrode is taken as 0.00 V at all temperature.
- It is a reversible electrode.
- It is used as a reference electrode.
- A saturated calomel electrode is also used as a secondary reference electrode. It has a potential of -0.24 volt.

### 8. Electrode Potential or Single Electrode Potential:

It is the tendency of an electrode to accept or to lose electrons.

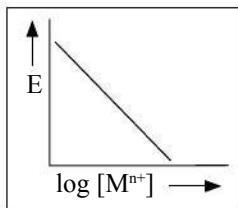
When a metal strip M is placed in contact with the solution of its own ions M<sup>n+</sup>, an electrical potential difference is set up between the metal strip and the solution due to either of the two tendencies.



- The electrical potential difference between metal strip and solution is known as half cell electrode potential (E).
  - Single electrode potential cannot be measured experimentally.
  - The potential difference between two single electrodes can be measured by using Potentiometer.
  - The tendency of oxidation can be represented by oxidation potential (E<sub>oxi</sub>).
  - The tendency of reduction can be represented by reduction potential (E<sub>red</sub>).
  - Oxidation potential of element is same in magnitude but opposite in sign to the reduction potential, that is, (E<sub>red</sub> = -E<sub>oxi</sub>). Therefore, by conventions, the electrode potentials (E) are represented by their reduction potentials E<sub>red</sub>.
  - E<sub>red</sub> values vary with the concentration of the ions in solution at particular temperature. The reduction potential of the electrode at standard state conditions (1 molar conc. of the ions, 298 K and 1 atm pressure) is called Standard reduction potential (E<sup>o</sup>).
  - The absolute values of E<sup>o</sup> for any electrode can not be determined because it is impossible to work with single half cell hence the E<sup>o</sup> values are determined with respect to standard hydrogen electrode (SHE) whose standard electrode potential (E<sup>o</sup>) is taken to be zero by conventions.
  - E<sup>o</sup> is an intensive property like temperature or molar volume. This means that E<sup>o</sup> is same for half cell reaction whether it is represented as  $2X^+ + 2e^- \rightarrow X_2$  or  $X^+ + e^- \rightarrow \frac{1}{2} X_2$ .
  - E<sup>o</sup> values are not thermodynamic functions and may not be added directly. However, they can be calculated from free energy which is extensive property.
- The value of electrode potential developed on an electrode depends upon**
- Temperature of the system.
  - Concentration of ions in solutions.
  - Chemical nature of the metal or non metal
  - Number of electrons transferred in the half cell reaction
  - It does not depend upon length of electron.

## Types Of Electrode Potential

**(i) Oxidation Potential:** When electrode is negatively charged with respect to solution then it acts as anode and oxidation takes place here.



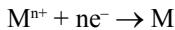
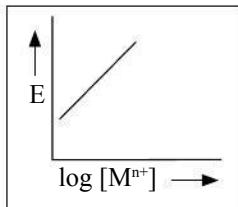
$$E_{\text{ox}} = E_{\text{ox}}^{\circ} - \frac{2.303 RT}{nF} \cdot \log_{10} [M^{n+}]$$

Here

$$\text{Intercept} = E_{\text{ox}}^{\circ}$$

$$\text{Slope} = \frac{-2.303 RT}{nF}$$

**(ii) Reduction potential:** When electrode is positively charged with respect to solution then it acts as cathode and reduction takes place here.



$$E_{\text{red}} = E_{\text{red}}^{\circ} - \frac{2.303 RT}{nF} \log_{10} \frac{1}{[M^{n+}]} .$$

$$E_{\text{red}} = E_{\text{red}}^{\circ} + \frac{2.303 RT}{nF} \log_{10} [M^{n+}]$$

Here

$$\text{Intercept} = E_{\text{red}}^{\circ}$$

$$\text{Slope} = \frac{2.303 RT}{nF}$$

## EMF of the Cell or Cell Voltage

It is the potential difference between the two terminals of the cell when no current is drawn from it. It is measured with the help of potentiometer or vacuum tube voltmeter.

## Calculation of the EMF of the Cell

Mathematically, it may be expressed as

$$E_{\text{cell}} \text{ or } \text{EMF} = [E_{\text{red}} (\text{cathode}) - E_{\text{red}} (\text{anode})]$$

$$E_{\text{cell}}^{\circ} \text{ or } \text{EMF}^{\circ}$$

$$= [E_{\text{red}}^{\circ} (\text{cathode}) - E_{\text{red}}^{\circ} (\text{anode})]$$

- For cell reaction to occur the  $E_{\text{cell}}$  should be positive. This can happen only if  $E_{\text{red}} (\text{cathode}) > E_{\text{red}} (\text{anode})$ .
- $E_{\text{cell}}^{\circ}$  must be positive for a spontaneous reaction.
- Rate of reaction is directly proportional to the emf of the cell.
- The emf of the cell depends on the intensity of the reaction in the cell.
- It measures free energy change for maximum convertibility of heat into useful work.
- It causes flow of current from higher value of  $E^{\circ}$  electrode to lower  $E^{\circ}$  value electrode.

## Difference between EMF and Cell Potential

EMF	Cell potential
It is measured by potentiometer.	It is measured by voltmeter.
It is potential difference between two electrodes when no current is flowing in the circuit	It is potential difference between two electrodes when current is flowing through the circuit
It is maximum voltage obtained from cell	It is less than maximum voltage
It corresponds to maximum useful work obtained from galvanic cell.	It does not correspond.

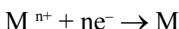
## Nernst Equation

This equation gives the relationship between electrode potential and concentration of ions in the solution.

Or

It shows the dependency of electrode potential on the concentration of the ions with which the electrode is reversible.

For a single electrode involving the reduction process,



The Nernst equation is

$$E = E^\circ + \frac{2.303 RT}{nF} \log_{10} \frac{[M^{n+}]}{[M]}$$

or

$$E = E^\circ - \frac{2.303 RT}{nF} \log_{10} \frac{[M]}{[M^{n+}]}.$$

At 25°C or 298 K

$$E = E^\circ + \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log_{10} \frac{[M^{n+}]}{[M]}$$

$$E = E^\circ + \frac{0.059}{n} \log_{10} \frac{[M^{n+}]}{[M]}$$

or

$$E = E^\circ - \frac{0.059}{n} \log_{10} \frac{[M]}{[M^{n+}]}.$$

Here R = Gas constant

T = Absolute temperature

$E^\circ$  = emf of the cell

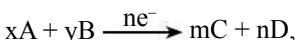
E = Electrode potential of cell

F = Faraday number

n = number of electrons transferred

■ If electrode is solid its active mass is taken as one.

■ For an electrochemical cell having net reaction



The emf can be calculated as

$$E_{cell} = E^\circ_{cell} + \frac{0.059}{n} \log \frac{[A]^x [B]^y}{[C]^m [D]^n}$$

In using the above equation, the following facts should be kept in mind.

■ Concentration or activity of gases is expressed in terms of their partial pressures.

■ n, the number of electrons transferred should be calculated from the balanced net cell reaction

■ Concentration or activity of solids is taken to be unity.

## Equilibrium Constant and Cell Potential

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log Q$$

At equilibrium

$$E_{cell} = 0, Q = K$$

$$0 = E^\circ_{cell} - \frac{0.0591}{n} \log_{10} K$$

$$\log_{10} K = \frac{E^\circ_{cell} \cdot n}{0.0591}.$$

■ **Relationship between free energy change ( $\Delta G$ ) and cell potential (E):** Electrical work done in one second is equal to electrical potential multiplied by total charge passed. If we want to obtain maximum work from a galvanic cell then charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore, if the emf (it is the potential of the cell when no current is drawn) of the cell is E and nF is the amount of charge passed and  $\Delta G$  is the Gibbs energy of the reaction then

$$\Delta G = -nF E_{cell}$$

for standard state conditions,

$$\Delta G^\circ = -nF E^\circ_{cell}$$

## Thermodynamics Relationship of Cell

### (i) Gibbs-Helmholtz equation:

$$\Delta G = \Delta H + T \left( \frac{\partial}{\partial T} \Delta G \right)_P$$

Here  $\Delta H$  = Change in enthalpy

T = Temperature

### (ii) Temperature Coefficient:

$$\Delta G = \Delta H + T \left( \frac{\partial}{\partial T} \Delta G \right)_P$$

$$-nFE_{cell} = \Delta H + T \left[ \frac{\partial}{\partial T} (-nF E_{cell}) \right]_P$$

$$\Delta H = -nF E_{cell} + nFT \left( \frac{\partial}{\partial T} E_{cell} \right)_P$$

$$\left( \frac{\partial}{\partial T} E_{cell} \right)_P = \text{Temperature coefficient}$$

### (iii) Change in Entropy:

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G - \Delta H = -T\Delta S \quad \dots \dots \text{(i)}$$

$$\Delta G = \Delta H + T \left( \frac{\partial}{\partial T} \Delta G \right)_P$$

$$\Delta G - \Delta H = T \left( \frac{\partial}{\partial T} \Delta G \right)_P \quad \dots \dots \text{(ii)}$$

From equation (i) and (ii), we get

$$-\Delta S = T \left( \frac{\partial}{\partial T} \Delta G \right)_P$$

$$\Delta S = - \left( \frac{\partial}{\partial T} \Delta G \right)_P$$

$$\Delta S = +nF \left( \frac{\partial}{\partial T} E_{cell} \right)_P$$

## Concentration Cells

Concentration cell is one in which emf arises as a result of different concentrations of the same electrolyte in the component half-cells.

- The two solutions are connected by a salt bridge and the electrodes are joined by a piece of metallic wire.
- The reduction occurs in the more concentrated compartment while oxidation occurs in the diluted compartment.

$$E = E^\circ - \frac{2.303 RT}{nF} \log \frac{[C_2]}{[C_1]}$$

or

$$E = E^\circ + \frac{2.303 RT}{nF} \log \frac{[C_1]}{[C_2]}$$

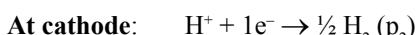
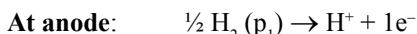
Concentration cells are of following two types:

- Electrode concentration cell
- Electrolyte concentration cell

**(i) Electrode Concentration Cell:** When emf is produced between two similar electrodes at different concentrations dipped in the same solution of electrolyte.



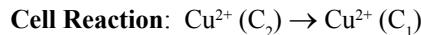
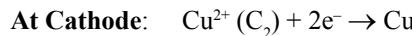
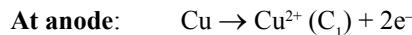
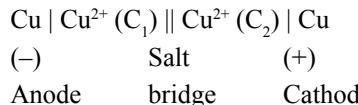
Anode            Cathode



$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{1} \log_{10} (p_2/p_1)^{1/2}$$

$$E_{cell} = \frac{0.0591}{2} \cdot \log_{10} \frac{p_1}{p_2}$$

**(ii) Electrolyte Concentration Cell:** When identical electrodes are dipped into the solutions of same electrolyte of different concentration, emf produced due to the difference in concentration is called liquid-junction potential. This type of cell is called electrolyte concentration cell.

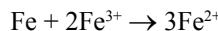


$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \cdot \log_{10} \frac{C_2}{C_1}$$

$$E_{cell} = \frac{0.0591}{2} \log_{10} \frac{C_2}{C_1}$$

## Illustrations

13. If  $E^\circ_{Fe^{2+}/Fe} = -0.441$  V and  $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.771$  V, the standard EMF of the reaction will be



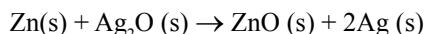
**Solution**  $E^\circ_{Fe^{2+}/Fe} = -0.441$  V

$$E^\circ_{Fe^{3+}/Fe^{2+}} = 0.771$$
 V

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{OPFe/Fe^{2+}} + E^\circ_{RPFe^{3+}/Fe^{2+}} \\ &= +0.441 + 0.771 = 1.212 \text{ V} \end{aligned}$$

## Illustrations

14. For a Ag-Zn button cell, net reaction is



$$\Delta G_f^\circ(Ag_2O) = -11.21 \text{ kJ mol}^{-1}$$

$$\Delta G_f^\circ(ZnO) = -318.3 \text{ kJ mol}^{-1}$$

Find the  $E^\circ_{cell}$  of the button cell here.

**Solution**  $\Delta G^\circ = \Delta G_f^\circ(ZnO) - \Delta G_f^\circ(Ag_2O)$

$$= -318.30 + 11.21 = -307.09 \text{ kJ}$$

$$= -307.09 \times 10^3 \text{ J}$$

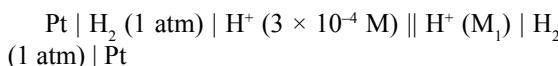
$$\Delta G^\circ = -nFE^\circ_{cell}$$

$$-307.09 \times 10^3 = -2 \times 96500 \times E^\circ_{cell}$$

$$E^\circ_{cell} = 1.591 \text{ V}$$

## Illustrations

15. The observed emf of the cell



is 0.154 V. Calculate the value of  $\text{M}_1$  and pH of cathodic solution.

**Solution**  $E_{\text{cell}} = 0.0591 \log_{10} \frac{\text{M}_1}{3 \times 10^{-4}}$ .

$$\log_{10} \frac{\text{M}_1}{3 \times 10^{-4}} = \frac{0.154}{0.0591} = 2.6058$$

$$\frac{\text{M}_1}{3 \times 10^{-4}} = 4.034 \times 10^2$$

$$\text{M}_1 = 4.034 \times 10^2 \times 3 \times 10^{-4} \text{ M}$$

$$= 0.121 \text{ M}$$

$$\text{pH} = -\log_{10} [\text{H}^+] = -\log_{10} 0.121 = 0.917$$

16. Calculate the cell potential for the cell containing 0.10 M  $\text{Ag}^+$  and 4.0 M  $\text{Cu}^{2+}$  at 298 K.

Given  $E^\circ \text{Ag}^+/\text{Ag} = 0.80 \text{ V}$

$$E^\circ \text{Cu}^{2+}/\text{Cu} = 0.34 \text{ V}$$

**Solution**  $\text{Cu} \text{ (s)} \mid \text{Cu}^{2+} (4.0 \text{ M}) \parallel \text{Ag}^+ (0.1 \text{ M}) \mid \text{Ag} \text{ (s)}$

Here  $n = 2$ ;

$$\begin{aligned} E &= E_{\text{cell}}^\circ + \frac{0.0591}{2} \log \frac{[\text{Ag}^+]^2}{[\text{Cu}^{2+}]} \\ &= 0.80 - 0.34 + \frac{0.0591}{2} \log_{10} \frac{[0.1]^2}{[4.0]} \\ &= 0.46 + 0.0295 \times \log_{10} 2.5 \times 10^{-3} \\ &= 0.46 - 0.07676 = 0.3832 \text{ V} \end{aligned}$$

17. Calculate the e.m.f of the following cell at 298 K.



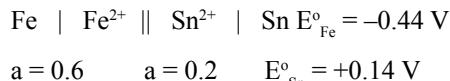
Given:  $E^\circ \text{Zn}^{2+}/\text{Zn} = -0.76 \text{ C}$

$$E^\circ \text{Ag}^+/\text{Ag} = +0.80 \text{ V}$$

**Solution**  $E_{\text{cell}} = E_{\text{cell}}^\circ + \frac{0.0591}{n} \log \frac{[\text{Ag}^+]^2}{[\text{Zn}^{2+}]}$

$$\begin{aligned} &= 0.80 - (-0.76) + \frac{0.0591}{2} \log_{10} \frac{[0.01]^2}{[0.1]} \\ &= 1.56 + \frac{0.0591}{2} \log_{10} 1 \times 10^{-3} \\ &= 1.56 - 0.08865 = 1.471 \text{ V} \end{aligned}$$

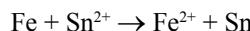
18. Find the EMF of the following cells:



**Solution**  $\text{Fe} \mid \text{Fe}^{2+} \parallel \text{Sn}^{2+} \mid \text{Sn}$

$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{R}}^\circ - E_{\text{L}}^\circ \\ &= 0.14 - (-0.44) = 0.58 \text{ V} \end{aligned}$$

Cell reaction



According to Nernst's equation,

$$\begin{aligned} E &= E^\circ - \frac{0.059}{N} \log_{10} \frac{[\text{Fe}^{2+}]}{[\text{Sn}^{2+}]} \\ &= 0.58 - \frac{0.059}{2} \log_{10} \frac{0.6}{0.2} \\ &= 0.58 - 0.0295 \log_{10} 3 \\ &= 0.58 - 0.0295 \times 0.4771 \\ &= 0.58 - 0.014 \\ &= 0.566 \text{ V} \end{aligned}$$

19. Find the pH of the following half-cell



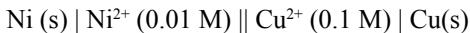
The oxidation electrode potential = 0.3 V.

**Solution**  $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$

$$E = E^\circ - \frac{0.059}{N} \log_{10} \frac{[\text{H}^+]^2}{[\text{H}_2]}$$

$$\begin{aligned} 0.3 &= 0 - \frac{0.059}{2} \log_{10} [\text{H}^+]^2 \\ - \log [\text{H}^+] &= \frac{0.3}{0.059} = 5.08 \\ \text{pH} &= 5.08 \end{aligned}$$

20. Calculate the cell potential of the given cell at 25°C. ( $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $F = 96500 \text{ C mol}^{-1}$ ).



Given:  $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$

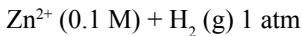
$E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V}$

**Solution**  $E_{\text{cell}} = E_{\text{cell}}^\circ + \frac{2.303 \text{ RT}}{\text{nF}} \log_{10} \frac{[\text{Cu}^{2+}]}{[\text{Ni}^{2+}]}$

$$= 0.34 - (-0.25) + \frac{2.303 \times 8.31 \times 298}{2 \times 96500} \log \frac{0.1}{0.01}$$

$$= 0.59 + \frac{0.0591}{2} \log_{10} 10 = 0.6195 \text{ V}$$

21. The emf of a cell corresponding to the reaction,



is 0.28 volt at 25°C. Write the half cell reactions and calculate the pH of the solution at the hydrogen electrode.

$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ volt}$

$E^\circ_{\text{H}^+/\text{H}_2} = 0$

**Solution**  $E_{\text{cell}}^\circ = 0.76 \text{ volt}$

According to Nernst equation,

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{2} \log_{10} \frac{[\text{Zn}^{2+}][\text{H}_2]}{[\text{H}^+]^2}$$

$$0.28 = 0.76 - \frac{0.0591}{2} \log_{10} \frac{(0.1) \times 1}{[\text{H}^+]^2}$$

$$\log_{10} \frac{0.1}{[\text{H}^+]^2} = \frac{2 \times 0.48}{0.0591}$$

$$\log_{10} 0.1 - \log_{10} [\text{H}^+]^2 = 16.2436$$

$$[\text{As} - \log_{10} [\text{H}^+]] = \text{pH}$$

$$2 \text{ pH} = 16.2436 - \log_{10} 0.1$$

$$\text{pH} = \frac{17.2436}{2} = 8.6218$$

22. A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution

of  $10^{-6} \text{ M}$  hydrogen ions. The EMF of the cell is  $0.118 \text{ V}$  at  $25^\circ\text{C}$ . Calculate the concentration of hydrogen ions at the positive electrode.

**Solution** Suppose  $[\text{H}^+]$  at the cathode =  $X \text{ mol litre}^{-1}$

$$E_2 = E^\circ + 0.059 \log_{10} X \quad \dots \dots \text{ (i)}$$

$$E_1 = E^\circ + 0.059 \log_{10} 10^{-6} \quad \dots \dots \text{ (ii)}$$

Subtracting equation (ii) from (i),

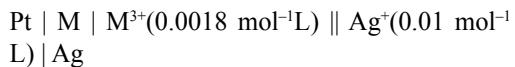
$$E_2 - E_1 = 0.059 (\log_{10} X - \log_{10} 10^{-6})$$

$$0.118 = 0.059 (\log_{10} X + 6)$$

$$X = 10^{-4}$$

$$[\text{H}^+] = 10^{-4} \text{ mole litre}^{-1}$$

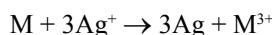
23. To find the standard potential of  $\text{M}^{3+}/\text{M}$  electrode, the following cell is constituted:



The emf of this cell is found to be 0.42 volt. Calculate the standard potential of the half reaction.



**Solution** The cell reaction is



According to Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{3} \log_{10} \frac{[\text{M}^{3+}]}{[\text{Ag}^+]^3}.$$

$$0.42 = E_{\text{cell}}^\circ - \frac{0.0591}{3} \log_{10} \frac{(0.0018)}{(0.01)^3}$$

$$= E_{\text{cell}}^\circ - 0.064$$

$$E_{\text{cell}}^\circ = (0.42 + 0.064) = 0.484 \text{ volt}$$

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

$$E_{\text{anode}}^\circ = E_{\text{cathode}}^\circ - E_{\text{cell}}^\circ$$

$$= (0.80 - 0.484) = 0.32 \text{ volt.}$$

**ELECTROCHEMICAL SERIES**

Reaction (oxidized form)	Reduced form	$\epsilon^\circ/V$
$\text{Li}^+ + \text{e}^-$	$\text{Li}(\text{s})$	-3.05
$\text{K}^+ + \text{e}^-$	$\text{K}(\text{s})$	-2.93
$\text{Ca}^{2+} + 2\text{e}^-$	$\text{Ca}(\text{s})$	-2.87
$\text{Na}^+ + \text{e}^-$	$\text{Na}(\text{s})$	-2.71
$\text{Mg}^{2+} + 2\text{e}^-$	$\text{Mg}(\text{s})$	-2.36
$\text{Al}^{3+} + 3\text{e}^-$	$\text{Al}(\text{s})$	-1.66
$\text{Zn}^{2+} + 2\text{e}^-$	$\text{Zn}(\text{s})$	-0.76
$\text{Cr}^{3+} + 3\text{e}^-$	$\text{Cr}(\text{s})$	-0.74
$\text{Fe}^{2+} + 2\text{e}^-$	$\text{Fe}(\text{s})$	-0.44
$\text{Ni}^{2+} + 2\text{e}^-$	$\text{Ni}(\text{s})$	-0.25
$\text{Sn}^{2+} + 2\text{e}^-$	$\text{Sn}(\text{s})$	-0.14
$\text{Pb}^{2+} + 2\text{e}^-$	$\text{Pb}(\text{s})$	-0.13
$2\text{H}^+ + 2\text{e}^-$	$\text{H}_2(\text{g})$	0.00
$\text{AgBr}(\text{s}) + \text{e}^-$	$\text{Ag}(\text{s}) + \text{Br}^-$	0.10
$\text{AgCl}(\text{s}) + \text{e}^-$	$\text{Ag}(\text{s}) + \text{Cl}^-$	0.22
$\text{Cu}^{2+} + 2\text{e}^-$	$\text{Cu}(\text{s})$	0.34
$\text{Cu}^+ + \text{e}^-$	$\text{Cu}(\text{s})$	0.52
$\text{I}_2 + 2\text{e}^-$	$2\text{I}^-$	0.54
$\text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^-$	$\text{H}_2\text{O}_2$	0.68
$\text{Fe}^{3+} + \text{e}^-$	$\text{Fe}^{2+}$	0.77
$\text{Ag}^+ + \text{e}^-$	$\text{Ag}(\text{s})$	0.80
$2\text{Hg}^{2+} + 2\text{e}^-$	$\text{Hg}_{2}^{2+}$	0.92
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^-$	$\text{NO}(\text{g}) + 2\text{H}_2\text{O}$	0.97
$\text{Br}_2 + 2\text{e}^-$	$2\text{Br}^-$	1.09
$\text{MnO}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^-$	$\text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.23

$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^-$	$2\text{H}_2\text{O}$	1.23
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^-$	$2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33
$\text{Cl}_2(\text{g}) + 2\text{e}^-$	$2\text{Cl}^-$	1.36
$\text{Au}^{3+} + 3\text{e}^-$	$\text{Au}(\text{s})$	1.40
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^-$	$\text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$	$2\text{H}_2\text{O}$	1.78
$\text{Co}^{3+} + \text{e}^-$	$\text{Co}^{2+}$	1.81
$\text{F}_2(\text{g}) + 2\text{e}^-$	$2\text{F}^-$	2.87
Decreasing strength of oxidising agent	Decreasing strength of reducing agent	

It is the arrangement of various electrodes or elements in the increasing order of their standard reduction potential or decreasing order of their standard oxidation potential. It is called electromotive or activity series of the elements

**Features of Electrochemical Series**

- Metals with positive  $E_{op}^\circ$  or negative  $E_{rp}^\circ$  are strongly electro positive and have more reactivity. It means a lower placed element or metal is replaced by upper placed or higher element while higher element can be coated by lower metal.

Example, (i)  $\text{Zn} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu}$

Here Cu is replaced by Zn due to more oxidation potential or reactivity of Zn, while Zn is coated by Cu.

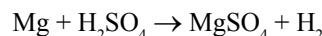
Zn – Cu couple is also coated by Cu. Here, solution turns from blue to colourless and rod becomes reddish brown from Gray white.

(ii)  $\text{Cu} + 2\text{AgNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{Ag}$

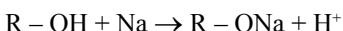
Here solution becomes colourless to blue and rod becomes reddish brown to white.

- Metals above  $\text{H}_2$  can easily replace  $\text{H}_2$  from acid, bases etc. due to there more positive  $E_{op}^\circ$  or reactivity

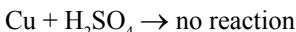
For example,



$E^\circ_{O.P.}$  of Mg >  $E^\circ_{O.P.}$  of H<sub>2</sub>



- Lower placed metals (Cu, Hg, Ag, Pt, Au) to H<sub>2</sub> can not do that as  $E^\circ_{O.P.}$  of H<sub>2</sub> is more than their  $E^\circ_{op}$



- Oxides of lower metals (Cu, Hg, Ag, Pt, Au) are easily reduced by H<sub>2</sub> or Carbon as they are unstable thermally due to positive  $E^\circ_{op}$  they also decomposed on heating.

- More  $E^\circ_{O.P.}$  means ease of tendency to oxidize that is, reducing agents while more  $E^\circ_{R.P.}$  means ease to be reduced that is, oxidizing agents. It means metal above hydrogen having positive  $E^\circ_{O.P.}$  are reducing agents.

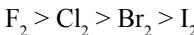
Reducing property  $\propto E^\circ_{O.P.}$

For example, Li is the strongest reducing agent due to maximum  $E^\circ_{O.P.}$

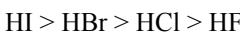
For example, If for A is  $E^\circ_{O.P.}$  is -0.44 V and for B, E is -0.28 V than A is better reducing agent than B.

- Metals (Cu, Hg, Ag, Pt, Au) having high  $E^\circ_{R.P.}$  are oxidizing agents. and they have tendency to be reduced

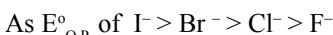
For example, Oxidizing power  $\propto E^\circ_{R.P.}$



Oxidizing power decreases



Reducing power decreases



- Elements with more positive  $E^\circ_{R.P.}$  will be discharged first at cathode i.e., discharging order increases from Li to F (for M<sup>+</sup>).

Increasing order of deposition of some cation

Li<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, Zn<sup>2+</sup>, Fe<sup>2+</sup>, H<sup>+</sup>, Cu<sup>2+</sup>, Ag<sup>+</sup>, Au<sup>3+</sup>

- In case of negative ions, anion with stronger reducing nature is discharged first at anode

Discharging order  $\propto \frac{1}{\text{Value of } E^\circ_{R.P.}}$

Increasing order of discharge of some anion



- Hydroxides of upper metals are strongly basic and their salts do not undergo hydrolysis while

hydroxides of lower metals are weakly acidic and their salts undergo hydrolysis.

## Enhance Your Knowledge

### Primary Cells

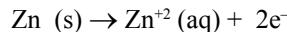
- In such cells redox reaction occurs only once so cells can not be recharged again.
- The Cell become dead after some time as electrode reactions cannot be reversed.  
Example, Dry cell, mercury cell

### Dry Cell

- It is compact form of Lechlanche cell.
- It has anode of Zn-container and cathode of graphite rod surrounded by MnO<sub>2</sub> + Carbon.
- Here a paste of NH<sub>4</sub>Cl and ZnCl<sub>2</sub> is filled in between the electrodes.

### Cell Reactions

#### At anode



#### At cathode



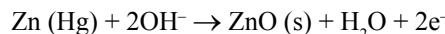
- Zn<sup>2+</sup> combines with NH<sub>3</sub> to form diammine Zn(II) cation.
- Dry cell has short life as NH<sub>4</sub>Cl (acidic) corrodes the Zn-container even if the cell is not in use.
- The cell potential is 1.25 to 1.5 volt

### Mercury Cell

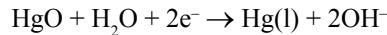
- In commonly used mercury cell the reducing agent is zinc and the oxidizing agent is mercury (II) oxide.

#### Cell Reactions

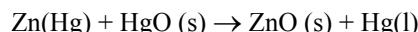
##### At anode:



##### At cathode:



The overall reaction is



## 6.20 ■ Electrochemistry

- The cell potential is approximately 1.35 V and remains constant throughout its life as overall reaction does not involve any ion, whose concentration can change during its life time. It is used in hearing aids, watches etc.

### Secondary Cell

- It can be recharged by passing current to use again as electrode reactions are reversible. Example, lead storage battery, Ni-Cd storage cell.

### Batteries

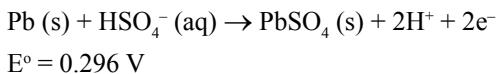
Electrochemical cell used as battery. The voltage provided by the battery is sum of individual voltage of cells.

**Types of Batteries:** Batteries are of following types:

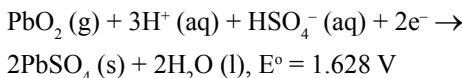
- (i) Lead Storage Batteries:** Six cells are connected in series each cell provided 2V so total volt provided by the battery is 12 V. The anode, a series of lead grids packed with spongy lead and cathode, a series of grids packed with lead dioxide 38% by weight  $\text{H}_2\text{SO}_4$  act as electrolyte.

### Cell reaction (When discharging takes place)

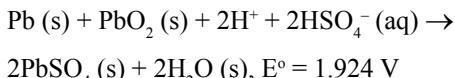
#### At anode:



#### At cathode:



#### Net reaction

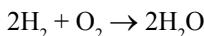


#### Nickel-Cadmium Cell:

- A rechargeable nickel-cadmium cell is a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide.

### Fuel Cell

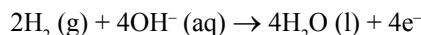
- The best example of fuel cell is Hydrogen–oxygen fuel cell



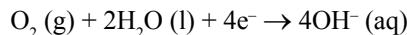
- Astronauts (Apollo moon flight) used  $\text{H}_2$ ,  $\text{O}_2$  fuel cell
- It is pollution free, continuous source of energy and highly efficient.

### Cell Reactions

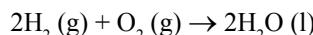
#### At anode



#### At cathode



Net reaction is



- Requirement:** It should have compactness, lightness, ruggedness and not much volume drop during use.

- The thermodynamic efficiency of fuel cells is the ratio of the electrical fee energy to the  $\Delta H$  of the reaction.

$$\eta = \frac{\Delta G}{\Delta H}$$

#### Rusting or Corrosion of Metals

It is the destruction of metal on reaction with environment. It is reverse extraction of metals and it is a redox process.

Example, Rust of iron is  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$



$\text{Fe}(\text{OH})_2$  dehydrates and oxidizes into  $\text{FeO}$   $\text{Fe}(\text{OH})_3$ , then finally into rust by dehydration.

- An electrochemical cell known as corrosion cell is developed at the surface of iron.

**Anode**-Pure iron

**Cathode**-impure surface

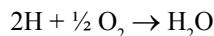
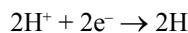
### Electrolyte



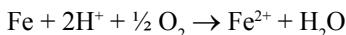
#### Anode reaction



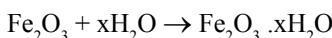
#### Cathode reaction



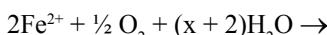
### Net reaction



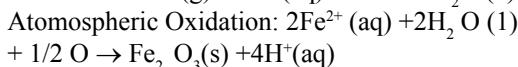
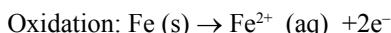
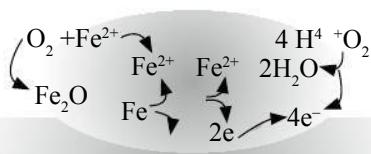
### At surface



Net reaction at surface



Rust



### Factors Promoting Corrosion

Reactivity of metal, presence of impurities, presence of air and moisture, strains in metal and presence of electrolyte etc.

### Prevention of Corrosion

**Sacrificial protection:** By covering the surface of iron with a layer of metal which is more active than iron thus prevents the iron from losing electrons (Plating metal with a thin layer of less easily oxidizable metal like Mg, Zn, Sn)

### Galvanization

- By covering iron with more active metal like zinc. The layer of Zn on the iron surface when comes in contact with moisture, oxygen and  $\text{CO}_2$  in air, a protective invisible thin layer of basic zinc carbonate  $\text{ZnCO}_3 \cdot \text{Zn}(\text{OH})_2$  is formed due to which the galvanized iron sheets lose their lustre and tends to protect it from further corrosion.

- Iron can be coated with Cu or by Sn. Now if the coating is broken, iron is exposed and being more reactive than iron, Cu and Sn corrode more rapidly.

### Electrical Protection

**Cathodic Protection** More electropositive metals like Zn, Mg or Al may be connected with the iron pipes buried in the moist soil, canals, storage tanks etc.

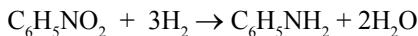
**Using Anti-rust Solutions** These are alkaline phosphate and alkaline chromate solutions. The alkaline nature of solutions prevents availability of  $\text{H}^+$  ions. On the surface of iron, a protective, insoluble thin film of iron phosphate is formed. These are used in car radiators etc., to prevent rusting.

### Solved Problems from the IITs

1. Calculate the electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50%. If the potential drop across the cell is 3.0 volt, how much energy will be consumed?

[IIT 1990]

**Solution** The reduction reaction is as follows:



123 g 6 g

1 mole 3 mole

Hydrogen required for reduction of 12.3/123 or 0.1 mole of nitrobenzene

$$= 0.1 \times 3 = 0.3 \text{ mole}$$

Amount of charge required for liberation of 0.3 mole of hydrogen

$$= 2 \times 96500 \times 0.3 = 57900 \text{ coulomb}$$

Actual amount of charge required as efficiency is 50%

$$= 2 \times 57900 = 115800 \text{ coulomb}$$

## 6.22 ■ Electrochemistry

$$\begin{aligned}\text{Energy consumed} &= 115800 \times 3.0 = 347400 \text{ J} \\ &= 347.4 \text{ kJ}\end{aligned}$$

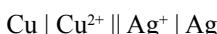
2. The standard reduction potential of  $\text{Cu}^{2+}/\text{Cu}$  and  $\text{Ag}^+/\text{Ag}$  electrodes are 0.337 and 0.799 volt respectively. Construct a galvanic cell using these electrodes so that its standard emf is positive. For what concentration of  $\text{Ag}^+$  will the emf of the cell at  $25^\circ\text{C}$  be zero if concentration of  $\text{Cu}^{2+}$  is 0.01 M?

[IIT 1990]

**Solution** Given  $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.337 \text{ V}$

$$E^\circ_{\text{Ag}^+/\text{Ag}} = 0.799 \text{ V.}$$

The standard emf will be positive if  $\text{Cu}/\text{Cu}^{2+}$  is anode and  $\text{Ag}^+/\text{Ag}$  is cathode. The cell may be represented as follows:



The cell reaction is as follows:



$$E^\circ_{\text{cell}} = \text{Oxidation Potential of anode} +$$

Reduction Potential of cathode

$$= -0.337 + 0.799$$

$$= 0.462 \text{ Volt}$$

According to Nernst equation,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log_{10} \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}.$$

$$\text{When } E_{\text{cell}} = 0$$

$$E^\circ_{\text{cell}} = \frac{0.0591}{2} \log_{10} \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}.$$

$$\log_{10} \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} = \frac{0.462 \times 2}{0.0591} = 15.6345$$

$$\frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} = 4.3102 \times 10^{15}$$

$$[\text{Ag}^+]^2 = \frac{0.01}{4.3102 \times 10^{15}}.$$

$$= 0.2320 \times 10^{-17}$$

$$= 2.320 \times 10^{-18}$$

$$[\text{Ag}^+] = 1.523 \times 10^{-9} \text{ M}$$

3. A current of 1.70 ampere is passed through 300 ml of 0.160 M solution of zinc sulphate for 230 seconds with a current efficiency of 90%. Calculate the molarity of  $\text{Zn}^{2+}$  ions after the

deposition of zinc. Assume the volume of the solution to remain constant during electrolysis.

[IIT 1991]

**Solution** Amount of charge passed =  $1.70 \times 230$  coulomb

Amount of actual charge passed

$$= \frac{90}{100} \times 1.70 \times 230$$

$$= 351.9 \text{ coulomb}$$

Number of moles of Zn deposited by passing 351.9 coulomb of charge

$$= \frac{1}{2 \times 96500} \times 351.9 = 0.000182$$

Molarity of  $\text{Zn}^{2+}$  ions after deposition of zinc

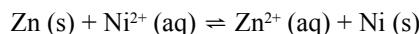
$$= [0.160 - \frac{0.000182 \times 1000}{300}] \text{ M}$$

$$= 0.154 \text{ M.}$$

4. Zinc granules are added in excess to 500 ml of 1.0 M nickel nitrate solution at  $25^\circ\text{C}$  until the equilibrium is reached. If the standard reduction potentials of  $\text{Zn}^{2+}/\text{Zn}$  and  $\text{Ni}^{2+}/\text{Ni}$  are  $-0.75$  and  $-0.24$  volt respectively, find out the concentration of  $\text{Ni}^{2+}$  ions in solution at equilibrium.

[IIT 1991]

**Solution** The reaction is



The cell involving this reaction would be



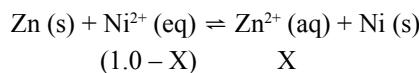
$$E^\circ_{\text{cell}} = -0.24 + 0.75 = 0.51 \text{ volt}$$

$$\log_{10} K_{\text{eq}} = \frac{nFE^\circ}{2.303 RT} = \frac{nE^\circ}{0.0591}.$$

$$= \frac{2 \times 0.51}{0.0591} = 17.25$$

$$\text{So } K_{\text{eq}} = 1.78 \times 10^{17}$$

Suppose 'X' is the concentration of  $\text{Ni}^{2+}$  that have been reduced to nickel at equilibrium.

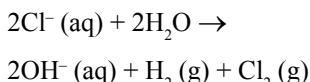


$$K_{\text{eq}} = \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]} = \frac{X}{(1-X)} = 1.78 \times 10^{17}$$

$$X = 1.0 \text{ M.}$$

$$\text{So } (1 - X) = [\text{Ni}^{2+}] = \frac{1.0}{1.78 \times 10^{17}} . \\ = 5.6 \times 10^{-18} \text{ M}$$

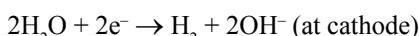
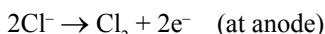
5. An aqueous solution of sodium chloride on electrolysis gives  $\text{H}_2$  (g),  $\text{Cl}_2$  (g) and  $\text{NaOH}$  according to the reaction:



A direct current of 25 ampere with a current efficiency 62% is passed through 20 litre of  $\text{NaCl}$  solution (20% of mass). Write down the reactions taking place at the anode and cathode. How long will it take to produce one kg of  $\text{Cl}_2$ ? What will be the molarity of the solution with respect to hydroxide ion? Assume no loss due to evaporation.

[IIT 1992]

**Solution** Reactions at anode and cathode are as follows:



$$1 \text{ Kg of Cl}_2 = \frac{1000}{71.0} = 14.08 \text{ mole}$$

Charge to produce one mole of  $\text{Cl}_2$

$$= 2 \times 96500 \text{ coulomb}$$

Charge to produce 14.08 mole of  $\text{Cl}_2$

$$= 2 \times 96500 \times 14.08 \text{ coulomb}$$

$$\text{Effective current} = \frac{62}{100} \times 25.0 = 15.5 \text{ ampere}$$

$$\text{Time} = \frac{\text{Charge}}{\text{Current}} .$$

$$= \frac{2 \times 96500 \times 14.08}{15.5}$$

$$= 175318.7 \text{ second} = 48.699 \text{ hour}$$

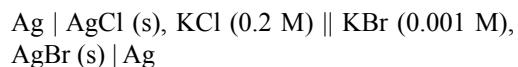
$\text{OH}^-$  ions produced = 2 × moles of  $\text{Cl}_2$

$$= 2 \times 14.08 = 28.16 \text{ mole}$$

$$\text{Molarity} = \frac{\text{Mole}}{\text{Volume}} .$$

$$= \frac{28.16}{20} = 1.408 \text{ M}$$

6. For the galvanic cell



Calculate the emf generated and assign correct polarity to each electrode for the spontaneous process after taking into account in the cell reaction at 25°C.

$$\text{Given, Ksp}_{\text{AgCl}} = 2.8 \times 10^{-10},$$

$$\text{Ksp}_{\text{AgBr}} = 3.3 \times 10^{-13}$$

[IIT 1992]

**Solution**  $E_{\text{cell}} = E$  (Oxidation potential of L.H.S electrode) +  $E$  (Reduction potential of R.H.S electrode)

$$= E^\circ (\text{Oxidation potential of Ag/Ag}^+) - 0.0591$$

$$\log [\text{Ag}^+]_{\text{L.H.S}} + E^\circ (\text{Reduction potential of Ag}^+/\text{Ag}) + 0.0591 \log [\text{Ag}^+]_{\text{R.H.S}}$$

$$= 0.0591 \log_{10} \frac{[\text{Ag}^+]_{\text{R.H.S}}}{[\text{Ag}^+]_{\text{L.H.S}}}$$

$$(\text{As } E^\circ \text{Ag/Ag}^+ + E^\circ \text{Ag}^+/\text{Ag} = 0)$$

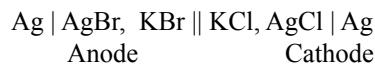
$$= 0.0591 \log_{10} \frac{\text{Ksp}_{\text{AgBr}} / [\text{Br}^-]}{\text{Ksp}_{\text{AgCl}} [\text{Cl}^-]}$$

$$= 0.0591 \log_{10} \frac{3.3 \times 10^{-13}}{0.001} \times \frac{0.2}{2.8 \times 10^{-10}} .$$

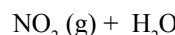
$$= -0.0371 \text{ volt}$$

As the cell potential is negative, so the cell reaction is non-spontaneous. For spontaneous reaction, emf should be positive.

Hence the correct cell reaction is as follows:



7. The standard reduction potential for the half cell having reaction,



$$\text{is } 0.78 \text{ volt.}$$

- (i) Calculate the reduction potential in 8  $\text{MH}^+$ .  
(ii) What will be the reduction potential of the half cell in a neutral solution?

## 6.24 ■ Electrochemistry

Assume all other species to be at unit concentration.

[IIT 1993]

$$\text{Solution } E_{\text{red}} = E^{\circ}_{\text{red}} + \frac{0.0591}{n} \log_{10} [\text{H}^+]^2$$

$$= 0.78 + \frac{0.0591}{2} \log_{10} (8)^2$$

$$= 0.78 + 0.0591 \times 3 \times 0.3010$$

$$= 0.833 \text{ volt}$$

$$(ii) \quad E_{\text{red}} = 0.78 + \frac{0.0591}{2} \log_{10} (10^{-7})^2$$

$$(\text{For neutral solution } [\text{H}^+] = 10^{-7} \text{ M})$$

$$= 0.78 - 0.0591 \times 7$$

$$= 0.367 \text{ volt.}$$

8. Chromium metal can be plated out from an acidic solution containing  $\text{CrO}_3$  according to the following reaction:  $\text{CrO}_3 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{Cr} + 3\text{H}_2\text{O}$

Calculate the mass of chromium plated out by 24000 coulomb. How long will it take to plate out 1.5 g of chromium using 12.5 ampere current?

[IIT 1993]

$$\text{Solution } \text{CrO}_3 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{Cr} + 3\text{H}_2\text{O}$$

$$\begin{array}{rcl} 6 \times 96500 & & 1 \text{ mole} \\ & & \\ C & & 52 \text{ g} \end{array}$$

Mass of chromium plated out by 24000 coulomb charge

$$= \frac{52}{6 \times 96500} \times 24000 = 2.155 \text{ g}$$

Charge required for plating out 1.5 g of chromium

$$= \frac{6 \times 96500}{52} \times 1.5 = 16701.92 \text{ coulomb}$$

$$\text{Time} = \frac{\text{Charge}}{\text{Current}}$$

$$= \frac{16701.92}{12.5} = 1336.15 \text{ second}$$

$$= 22.27 \text{ minute}$$

9. The standard reduction potential of  $\text{Ag}^+/\text{Ag}$  electrode at 298 K is 0.799 volt. Given for  $\text{AgI}$ ,  $K_{\text{sp}} = 8.7 \times 10^{-17}$ , evaluate the potential of the

$\text{Ag}^+/\text{Ag}$  electrode in a saturated solution of  $\text{AgI}$ . Also find the standard reduction potential of the  $\text{I}^-/\text{AgI}/\text{Ag}$  electrode.

[IIT 1994]

**Solution** In the saturated solution of  $\text{AgI}$ , the half cell reactions are



The cell reaction is



$$\text{So } [\text{Ag}^+]^2 = 8.7 \times 10^{-17}$$

$$[\text{Ag}^+] = \sqrt{(8.7 \times 10^{-17})} = 9.3 \times 10^{-9}$$

On putting the value of  $E^{\circ}_{\text{Ag}^+/\text{Ag}}$  and  $[\text{Ag}^+]$ , we get

$$E^{\circ}_{\text{Ag}^+/\text{Ag}} = 0.799 - 0.0591 \log_{10} (9.3 \times 10^{-9})$$

$$= 0.324 \text{ volt}$$

$$E^{\circ}_{\text{cell}} = 0.0591 \log_{10} K_{\text{sp}} (\text{AgI})$$

$$= 0.0591 \log_{10} (8.7 \times 10^{-17})$$

$$= -0.95 \text{ volt}$$

$E^{\circ}_{\text{cell}}$  = Oxidation potential of anode

+ Reduction potential of cathode

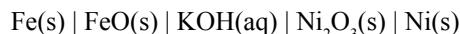
Reduction potential of cathode  $E^{\circ}_{\text{I}^-/\text{Ag}^+/\text{Ag}}$

$$= -0.95 - (-0.799)$$

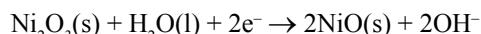
$$= -0.95 + 0.799$$

$$= -0.151 \text{ volt}$$

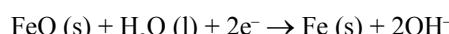
10. The Edison storage cell is represented as



The half cell reactions are:



$$E^{\circ} = +0.40 \text{ volt}$$



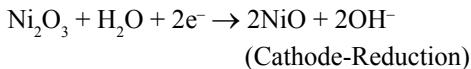
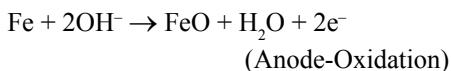
$$E^{\circ} = -0.87 \text{ volt}$$

(a) What is the cell reaction?

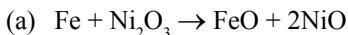
(b) What is the emf of the cell? How does it depend on the concentration of KOH?

- (c) What is the maximum amount of energy that can be obtained from one mole of  $\text{Ni}_2\text{O}_3$ ?  
[IIT 1994]

**Solution** Actual half reactions are:



So the cell reaction is:



$$(b) E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log_{10} \frac{[\text{NiO}]^2 [\text{FeO}]}{[\text{Fe}] [\text{Ni}_2\text{O}_3]} =$$

$$\text{Since } \frac{[\text{NiO}]^2 [\text{FeO}]}{[\text{Fe}] [\text{Ni}_2\text{O}_3]} = 1 \text{ as all are solids}$$

$$= 0.87 + 0.40 = 1.27 \text{ volt}$$

The emf of the cell is independent of KOH concentration.

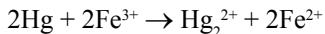
- (c) Maximum amount of electrical energy

$$= n F E^{\circ}$$

$$= 2 \times 96500 \times 1.27$$

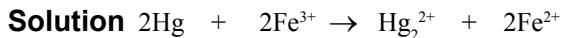
$$= 245.11 \text{ kJ}$$

11. An excess of liquid mercury is added to an acidified solution of  $1.0 \times 10^{-3} \text{ M}$   $\text{Fe}^{3+}$ . It is found that 5% of  $\text{Fe}^{3+}$  remains at equilibrium at  $25^\circ\text{C}$ . Calculate  $E^{\circ} \text{ Hg}_2^{2+}/\text{Hg}$  assuming that the only reaction that occurs is



(Given  $E\text{Fe}^{3+}/\text{Fe}^{2+} = 0.77 \text{ volt}$ )

[IIT 1995]



$$\text{At eq. Excess } \frac{10^{-3} \times 5}{100} \frac{10^{-3} \times 95}{2 \times 100} \frac{10^{-3} \times 95}{100}$$

$$\text{At eq. } E_{\text{cell}} = 0$$

$$0 = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log_{10} \frac{[\text{Hg}_2^{2+}] [\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2}$$

$$= (E^{\circ} \text{ Hg}/\text{Hg}_2^{2+} + E^{\circ} \text{ Fe}^{3+}/\text{Fe}^{2+})$$

$$-\frac{0.0591}{2} \log_{10} \frac{\frac{(10^{-3} \times 95)}{2 \times 100} (10^{-3} \times 95 \ 100)^2}{(10^{-3} \times 5 \ 100)^2}$$

$$E^{\circ} \text{Hg}/\text{Hg}_2^{2+} = -0.77 + \frac{0.0591}{2} \log_{10} \frac{(95)^3 \times 10^{-5}}{25 \times 2}$$

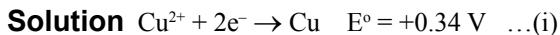
$$= -(0.77 + 0.0226)$$

$$= -0.7926 \text{ volt}$$

$$E^{\circ} \text{Hg}_2^{2+}/\text{Hg} = +0.7926 \text{ volt}$$

12. The standard reduction potential for  $\text{Cu}^{2+}/\text{Cu}$  is  $+0.34 \text{ V}$ . Find the reduction potential at pH = 14 for the above couple.  $K_{\text{sp}}$  of  $\text{Cu}(\text{OH})_2$  is  $1.0 \times 10^{-19}$ .

[IIT 1996]



For  $\text{Cu}(\text{OH})_2$

$$K_{\text{sp}} = 1.0 \times 10^{-19}$$

$$[\text{Cu}^{2+}] [\text{OH}^-]^2 = 1.0 \times 10^{-19}$$

As pH of the solution is 14

$$\text{So } [\text{OH}^-] = 1 \text{ M}$$

$$[\text{Cu}^{2+}] = 10^{-19}$$

According to Nernst's equation for (i)

$$E = E^{\circ} - \frac{0.059}{N} \log_{10} \frac{[\text{Cu}]}{[\text{Cu}^{2+}]}$$

$$= 0.34 - \frac{0.059}{2} \log_{10} \frac{1}{10^{-19}}$$

$$= 0.34 - \frac{0.059}{2} \times 19$$

$$= -0.22 \text{ V}$$

13. How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8.0 hours at a current of 8.46 amperes. What is the area of the tray if the thickness of the silver plating is  $0.00254 \text{ cm}$ ? Density of silver is  $10.5 \text{ g/cm}^3$ .

[IIT 1997]

**Solution** Mass of silver deposited ( $W$ ) =  $Z \times C \times t$

$$W = \frac{E \times C \times t}{F}$$

## 6.26 ■ Electrochemistry

(As  $Z = E/F$ )

$$W = \frac{107.8 \times 8.46 \times 8 \times 60 \times 60}{96500}$$

$$= 272.178 \text{ g}$$

$$\text{Volume of silver} = \frac{\text{Weight}}{\text{Density}}$$

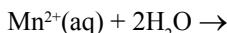
$$= \frac{272.178}{10.5} = 25.92 \text{ cc}$$

$$\text{Surface area} = \frac{\text{Volume}}{\text{Thickness}}$$

$$= \frac{25.92 \text{ cc}}{0.00254} \text{ cm}$$

$$= 10205.43 = 1.02 \times 10^4 \text{ cm}^2$$

14. Electrolysis of a solution of  $\text{MnSO}_4$  in aqueous sulphuric acid is a method for the preparation of  $\text{MnO}_2$  as per the reaction



Passing a current of 27 A for 24 hours gives one Kg of  $\text{MnO}_2$ . What is the value of current efficiency.

[IIT 1997]

**Solution** Wt. of  $\text{MnO}_2$  (w) =  $\frac{E \cdot I \cdot t}{F}$

$$1000 = \frac{87 \times I \times 24 \times 60 \times 60}{2 \times 96500}$$

$$I = 25.67 \text{ ampere}$$

$$\text{Current efficiency} = \frac{25.67 \times 100}{27} = 95\%$$

15. Calculate the equilibrium constant for the reaction:



Given:  $E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.44 \text{ V}$

$E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.68 \text{ V}$

[IIT 1997]

**Solution**  $\log K_C = \frac{n}{0.0591} \times E^\circ_{\text{cell}}$

$$= \frac{1}{0.0591} \times 0.76 = 12.8813$$

$K_C$  = antilog of 12.8813

$$K_C = 7.608 \times 10^{12}$$

16. Calculate the equilibrium constant for the reaction,  $2\text{Fe}^{3+} + 3\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_3^-$ . The standard

reduction potentials in acidic conditions are 0.77 and 0.54 V respectively for  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{I}_3^-/\text{I}^-$  couples.

[IIT 1998]

**Solution** Oxidation half  $3\text{I}^- \rightarrow \text{I}_3^- + 2\text{e}^-$

Reduction half  $[\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}] \times 2$

Cell reaction  $\text{Fe}^{3+} + 3\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_3^-$

Here  $n = 2$ ,  $E_{\text{cell}} = 0.77 - 0.54 = 0.23 \text{ V}$

According to Nernst equation,

$$E = E_{\text{cell}} - \frac{0.0591}{n} \log_{10} K_C$$

At equilibrium  $E = 0$

$$0 = 0.23 - \frac{0.0591}{2} \log_{10} K_C$$

On solving, we get

$$K_C = 6.26 \times 10^7$$

17. Find the solubility product of a saturated solution of  $\text{Ag}_2\text{CrO}_4$  in water at 298 K if the emf of the cell  $\text{Ag} | \text{Ag}^+$  (saturated  $\text{Ag}_2\text{CrO}_4$  solution) ||  $\text{Ag}^+$  (0.1 M) |  $\text{Ag}$  is 0.164 V at 298 K.

[IIT 1998]

**Solution**  $E_{\text{cell}} = \frac{0.0591}{1} \log_{10} \frac{[\text{Ag}^+]_{\text{R.H.S}}}{[\text{Ag}^+]_{\text{L.H.S}}}$

$$0.164 = \frac{0.0591}{1} \log_{10} \frac{0.1}{[\text{Ag}^+]_{\text{L.H.S}}}$$

$$[\text{Ag}^+]_{\text{L.H.S}} = 1.66 \times 10^{-4} \text{ M}$$

$$[\text{CrO}_4^{2-}] = \frac{1.66 \times 10^{-4}}{2}$$

$$K_{\text{sp}} (\text{Ag}_2\text{CrO}_4) = [\text{Ag}^+] [\text{CrO}_4^{2-}]$$

$$= (1.66 \times 10^{-4})^2 \times \frac{1.66 \times 10^{-4}}{2}$$

$$= 2.287 \times 10^{-12} \text{ mol}^3 \text{ L}^{-3}$$

18. The following electrochemical cell has been set up,

$\text{Pt}(1) | \text{Fe}^{3+}, \text{Fe}^{2+} (a=1) \parallel \text{Ce}^{4+}, \text{Ce}^{3+} (a=1) | \text{Pt}(2)$

$E^\circ (\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.77 \text{ V}$

$E^\circ (\text{Ce}^{4+}/\text{Ce}^{3+}) = 1.61 \text{ V}$

If an ammeter is connected between the two platinum electrodes, predict the direction of

flow of current. Will the current increase or decrease with time?

[IIT 2000]

**Solution** Current will flow from higher reduction potential electrode to lower reduction potential electrode, that is, from Pt (2) electrode to Pt (1) electrode.

$$E_{\text{cell}}^{\circ} = 1.61 - 0.77 = 0.84 \text{ volt}$$

19. Copper sulphate solution (250 ml) was electrolyzed using a platinum anode and a copper cathode. A constant current of 2 Ampere was passed for 16 minutes. It was found that after electrolysis the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with.

[IIT 2000]

**Solution** As number of Faraday passed through the aqueous solution of  $\text{CuSO}_4$

$$= \frac{I \times t}{96500} = \frac{(2 \times 10^{-3}) \times 16 \times 60}{96500} \\ = 1.98 \times 10^{-5}$$

So number of equivalents of  $\text{CuSO}_4$  involved in electrolysis from 1 litre solution

$$= 4 \times 1.98 \times 10^{-5} = 7.92 \times 10^{-5}$$

As after electrolysis, the absorbance reduces to 50% so initial number of equivalents of  $\text{CuSO}_4$  per litre

$$= 2 \times 7.92 \times 10^{-5}$$

$$= 1.584 \times 10^{-4}$$

Normality of  $\text{CuSO}_4$  solution =  $1.584 \times 10^{-4} \text{ N}$

20. The standard potential of the following cell is 0.23 V at 15°C and 0.21 V at 25°C

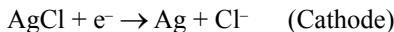
Pt H<sub>2</sub> (g) | HCl (aq) || AgCl (s) | Ag (s)

- (i) Write cell reaction.
- (ii) Calculate  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  for the cell reaction by assuming that these quantities remain unchanged in the range 15°C to 35°C.
- (iii) Calculate the solubility of AgCl in water at 25°C. Given the standard reduction potential of the  $\text{Ag}^+/\text{Ag}$  couple is 0.80 volt at 25°C.

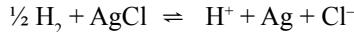
[IIT 2001]

## Solution

(i) Electrode process



Net reaction is:



(ii) As  $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

$$-22195 = \Delta H^{\circ} - 288 \times \Delta S^{\circ}$$

$$-20265 = \Delta H^{\circ} - 308 \times \Delta S^{\circ}$$

On solving we get

$$\Delta S^{\circ} = -96.5 \text{ J}$$

$$\Delta H^{\circ} = 49.987 \text{ kJ}$$

$$(iii) E = E^{\circ} - \frac{0.0591}{n} \log_{10} Q$$

At eq. E = 0, Q = K =  $[\text{Ag}^+] [\text{Cl}^-]$

$$0 = (0.8 - 0.22) + \frac{0.0591}{1} \log_{10} K_{\text{sp}}$$

$$\frac{(-0.8 + 0.22)}{0.0591} = \log_{10} K_{\text{sp}}$$

$$K_{\text{sp}} = 1.47 \times 10^{-10}$$

$$\text{Solubility (S)} = \sqrt{K_{\text{sp}}}$$

$$= \sqrt{(1.47 \times 10^{-10})}$$

$$= 1.21 \times 10^{-5} \text{ M}$$

21. Two students use same stock solution of  $\text{ZnSO}_4$  and a solution of  $\text{CuSO}_4$ . The emf of one cell is 0.03 V higher than that of other. The concentration of  $\text{CuSO}_4$  in the cell with higher emf value is 0.5 M. Calculate the concentration of  $\text{CuSO}_4$  in the other cell. ( $\frac{2.303 RT}{F} = 0.06$ )

[IIT 2003]

## Solution

Student I.

$\text{Zn (s)} | \text{ZnSO}_4 (\text{C}_1) || 0.5 \text{ M CuSO}_4 | \text{Cu (s)}$

$$E_1 = E^{\circ} - \frac{0.06}{2} \log_{10} \frac{C_1}{0.5} \quad \dots\dots(i)$$

Student II

$\text{Zn (s)} | \text{ZnSO}_4 (\text{C}_1) || \text{CuSO}_4 (\text{C}_2) | \text{Cu (s)}$

$$E_2 = E^{\circ} - \frac{0.06}{2} \log_{10} \frac{C_1}{C_2} \quad \dots\dots(ii)$$

## 6.28 ■ Electrochemistry

On subtracting equation (ii) from (i), we get

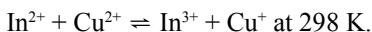
$$E_1 - E_2 = \frac{0.06}{2} \left[ \log_{10} \frac{C_1}{C_2} - \log_{10} \frac{C_1}{0.5} \right]$$

$$0.03 = \frac{0.06}{2} \left[ \log_{10} (0.5/C_2) \right]$$

$$1 = \log \frac{0.5}{2}$$

$$C_2 = 0.05 \text{ M}$$

22. Find the equilibrium constant for the reaction,



Given:  $E\text{Cu}^{2+}/\text{Cu}^+ = 0.15 \text{ V}$

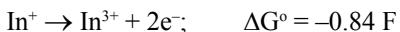
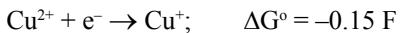
$$E^\circ \text{In}^{2+}/\text{In}^+ = -0.4 \text{ V}$$

$$E^\circ \text{In}^{3+}/\text{In}^+ = -0.42 \text{ V}$$

[IIT 2004]

### Solution

The given reversible reaction is obtained as follows:



The net reaction is



$$\text{As } \Delta G^\circ = -nFE^\circ$$

$$\text{So } -nFE^\circ = -0.59 \text{ F}$$

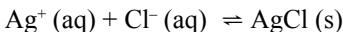
$$E^\circ = 0.59 \text{ volt}$$

Equilibrium constant is calculated as:

$$K = \text{antilog} \frac{nE^\circ}{0.059} .$$

$$= \text{antilog} \frac{1 \times 0.59}{0.059} = 10^{10}$$

23. For the reaction



Given:

$$\text{Species} \quad \Delta G_f^\circ (\text{kJ/mol})$$

$$\text{Ag}^+ (\text{aq}) \quad +77$$

$$\text{Cl}^- (\text{aq}) \quad -129$$

$$\text{AgCl} (\text{s}) \quad -109$$

Write the cell representation of above reaction and calculate  $E_{\text{cell}}^\circ$  at 298 K.

Also find the solubility product of AgCl.

- (b) If  $6.539 \times 10^{-2}$  g of metallic zinc is added to 100 ml saturated solution of AgCl. Find the value of  $\log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$ .

How many moles of Ag will be precipitate in the above reaction?

Given that:



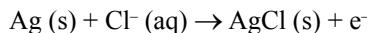
(Atomic mass of Zn = 65.39)

[IIT 2005]

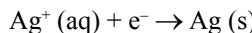
### Solution

The reaction is as follows:

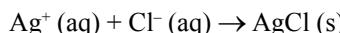
At anode:



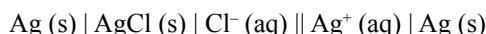
At cathode:



The net reaction is as follows:



Cell representation is as follows:



$$\begin{aligned} \Delta G^\circ &= \Delta G_f^\circ (\text{AgCl}) - [\Delta G_f^\circ (\text{Ag}^+) + \Delta G_f^\circ (\text{Cl}^-)] \\ &= -109 - (-129 + 77) \end{aligned}$$

$$= -57 \text{ kJ/mol} = -57000 \text{ J/mol}$$

$$\Delta G^\circ = -n F E_{\text{cell}}^\circ$$

$$-57000 = -1 \times 96500 \times E_{\text{cell}}^\circ$$

(as n = electrons transferred = 1)

$$E_{\text{cell}}^\circ = \frac{57000}{96500} = 0.59 \text{ volts}$$

$$E_{\text{cell}}^\circ = \frac{0.0591}{n} \log_{10} K_C$$

$$E_{\text{cell}}^\circ = \frac{0.0591}{n} \log_{10} \frac{[\text{AgCl}]}{[\text{Ag}^+] [\text{Cl}^-]}$$

$$E_{\text{cell}}^\circ = \frac{0.0591}{1} \log_{10} \frac{1}{K_{\text{sp}}}$$

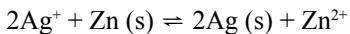
[As  $[\text{AgCl}] = 1$  and  $K_{\text{sp}} = [\text{Ag}^+] [\text{Cl}^-]$ ]

$$0.59 = -0.059 = \log_{10} K_{\text{sp}}$$

$$\log_{10} K_{sp} = -10$$

$$K_{sp} = 10^{-10}$$

- (b) When Zn is added to 100 ml of saturated AgCl solution.



$$E_{cell}^\circ = E^\circ \text{Ag}^+ | \text{Ag}(\text{s}) - E^\circ \text{Zn}^{2+} | \text{Zn}(\text{s})$$

$$= 0.80 - (-0.76) = 1.56 \text{ V}$$

$$E_{cell}^\circ = \frac{0.0591}{n} \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$$

$$1.56 = \frac{0.0591}{2} \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$$

$$\log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = 52.9$$

As the value of equilibrium constant is very high so the reaction moves in forward direction completely.

$$[\text{Ag}^+] = \sqrt{(10^{-10})} = 10^{-5}$$

$$(\text{As } K_{sp} = 10^{-10} = [\text{Ag}^+] [\text{Cl}^-])$$

$\text{Ag}^+$  in 100 ml of solution

$$= \frac{10^{-5} \times 100}{1000} = 10^{-6}$$

24. We have taken a saturated solution of AgBr.  $K_{sp}$  of AgBr is  $12 \times 10^{14}$ . If  $10^{-7}$  mole of  $\text{AgNO}_3$  are added to 1 litre of this solution find conductivity (specific conductance) of this solution in terms of  $10^{-7} \text{ S m}^{-1}$  units.

$$\text{Given } \lambda^\circ(\text{Ag}^+) = 6 \times 10^{-3} \text{ Sm}^2 \text{ mol}^{-1},$$

$$\lambda^\circ(\text{Br}^-) = 8 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1},$$

$$\lambda^\circ(\text{NO}_3^-) = 7 \times 10 \text{ S m}^2 \text{ mol}^{-1}.$$

[IIT 2006]

The solubility of AgBr in presence of  $10^{-7}$  molar  $\text{AgNO}_3$  is  $3 \times 10^{-7} \text{ M}$ .

Therefore  $[\text{Br}^-] = 3 \times 10^{-4} \text{ m}^3$ ,  $[\text{Ag}^+] = 4 \times 10^{-4} \text{ m}^3$  and  $[\text{NO}_3^-] = 10^{-4} \text{ m}^3$

$$\begin{aligned} \text{Therefore } K_{\text{total}} &= \text{KBr}^- + \text{KAg}^+ + \text{KNO}_3^- \\ &= 55 \text{ Sm}^{-1} \end{aligned}$$

## MULTIPLE-CHOICE QUESTIONS

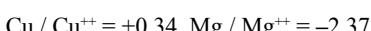
### Straight Objective Type Questions (Single Choice only)

1. The standard reduction potentials at 298 K for the following half reactions are given against each

$\text{Zn}^{2+}(\text{aq}) + 2\text{e} \leftrightarrow \text{Zn}(\text{s})$	-0.762
$\text{Cr}^{3+}(\text{aq}) + 2\text{e} \leftrightarrow \text{Cr}(\text{s})$	-0.740
$2\text{H}^+(\text{aq}) + 2\text{e} \leftrightarrow \text{H}_2(\text{g})$	0.000
$\text{Fe}^{3+}(\text{aq}) + 2\text{e} \leftrightarrow \text{Fe}^{2+}(\text{aq})$	0.770

Which is the strongest reducing agent?

- a.  $\text{H}_2(\text{g})$
  - b.  $\text{Cr}(\text{s})$
  - c.  $\text{Zn}(\text{s})$
  - d.  $\text{Fe}^{2+}(\text{aq})$
2. A solution containing one mole per litre of each  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{AgNO}_3$ ,  $\text{Hg}_2(\text{NO}_3)_2$ , is being electrolyzed by using inert electrodes. The values of standard electrode potentials in volts (reduction potentials) are



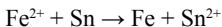
With increasing voltage, the sequence of deposition of metals on the cathode will be

- a. Cu, Hg, Ag
  - b. Ag, Hg, Cu, Mg
  - c. Mg, Cu, Hg, Ag
  - d. Ag, Hg, Cu
3. The reaction
- $$\frac{1}{2}\text{Hg}_2(\text{g}) + \text{AgCl}(\text{s}) = \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Ag}(\text{s})$$
- occurs in the galvanic cell
- a. Pt |  $\text{H}_2(\text{g})$  |  $\text{KCl}$  (solution) |  $\text{AgCl}$  (s) | Ag
  - b. Pt |  $\text{H}_2(\text{g})$  |  $\text{HCl}$  (solution) |  $\text{AgCl}$  (s) | Ag
  - c. Pt |  $\text{H}_2(\text{g})$  |  $\text{HCl}$  (solution) |  $\text{AgNO}_3$  (solution) | Ag
  - d. Ag |  $\text{AgCl}$  (s) |  $\text{KCl}$  (solution) |  $\text{AgNO}_3$  (solution) | Ag
4. An electrochemical cell reaction is: Pt,  $\text{H}_2$  (1 atm) |  $\text{HCl}$  (0.1 M) ||  $\text{CH}_3\text{COOH}$  (0.1 M) |  $\text{H}_2$  (1 atm), Pt. The emf of this cell will not be zero, because

- a. emf depends upon molarities of acids used
- b. pH of 0.1 M HCl and 0.1 M  $\text{CH}_3\text{COOH}$  is not same

- c. acids used in two compartments are different
- d. temperature is constant

5. When a lead storage battery is discharged
- a. lead is formed
  - b. lead sulphate is consumed
  - c.  $\text{SO}_2$  is evolved
  - d. sulphuric acid is consumed
6. The volume of gas measured at NTP, liberated at anode from the electrolysis of  $\text{Na}_2\text{SO}_4$  solution by a current of 5.0 Å passed for 3 minutes 13s.
- a. 224 ml
  - b. 112 ml
  - c. 56 ml
  - d. none of these
7. A solution of sodium sulphate in water is electrolyzed using inert electrodes. The products at the cathode and anode are respectively
- a.  $\text{O}_2, \text{H}_2$
  - b.  $\text{O}_2, \text{Na}$
  - c.  $\text{O}_2, \text{SO}_2$
  - d.  $\text{H}_2, \text{O}_2$
8. The standard oxidation potential  $E^\circ$  for the half reactions are as
- $$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-; E^\circ = +0.76 \text{ V}$$
- $$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-; E^\circ = +0.41 \text{ V}$$
- The EMF for the cell reaction
- $$\text{Fe}^{2+} + \text{Zn} \rightarrow \text{Zn}^{2+} + \text{Fe}$$
- a. +1.17 V
  - b. -0.35 V
  - c. +0.35 V
  - d. 0.117 V
9. At 25°C, the EMF of the cell
- $$\text{Pt}, \text{H}_2(1 \text{ atm}) | 10^{3+} \text{ M KOH} || 0.1 \text{ M HCl} | \text{H}_2(1 \text{ atm}), \text{Pt}$$
- is equal to
- a. +0.591 V
  - b. -1.182 V
  - c. +1.182 V
  - d. +10 V
10. When a copper wire is placed in a solution of  $\text{AgNO}_3$ , the solution acquires blue colour. This is due to the formation of
- a.  $\text{Cu}^+$  ions
  - b.  $\text{Cu}^{2+}$  ions
  - c. soluble complex of copper with  $\text{AgNO}_3$
  - d.  $\text{Cu}^-$  ion by the reduction of Cu.
11. The standard reduction potential for
- $$\text{Fe}^{2+}/\text{Fe}$$
- and
- $\text{Sn}^{2+}/\text{Sn}$
- electrodes are -0.44 and -0.14 volt respectively. For the cell reaction:



The standard emf is

- |                    |                    |
|--------------------|--------------------|
| <b>a.</b> +0.30 V  | <b>b.</b> -0.58 V  |
| <b>c.</b> + 0.58 V | <b>d.</b> -0.300 V |

12. A metal wire (M) dipped into 40 mL 1.0 M solution of its  $\text{M}^{2+}$  ion has a potential of 29.5 millivolt at 25°C. How much volume of water be added to the metal ion solution so that when it is combined with standard hydrogen electrode, no current flows?

- |                   |                  |
|-------------------|------------------|
| <b>a.</b> 1000 ml | <b>b.</b> 400 ml |
| <b>c.</b> 350 ml  | <b>d.</b> 0 ml   |

13. Of the following metals that cannot be obtained by the electrolysis of the aqueous solution of their salts are

- |                     |                     |
|---------------------|---------------------|
| <b>a.</b> Ag and Mg | <b>b.</b> Ag and Al |
| <b>c.</b> Mg and Al | <b>d.</b> Cu and Cr |

14. A certain current liberates 0.504 g of hydrogen in 2 hour. The amount (or mass) of copper deposited at the cathode during the electrolysis of  $\text{CuSO}_4$  (aq) solution by the same current flowing for the same time is (atomic masses H = 1.0, Cu = 63.5)

- |                  |                  |
|------------------|------------------|
| <b>a.</b> 16.0 g | <b>b.</b> 32.0 g |
| <b>c.</b> 8.6 g  | <b>d.</b> 1.60 g |

15. A solution of  $\text{Na}_2\text{SO}_4$  in water is electrolyzed using inert electrodes. The product at the cathode and the anode are respectively.

- |                                    |                                     |
|------------------------------------|-------------------------------------|
| <b>a.</b> $\text{O}_2, \text{H}_2$ | <b>b.</b> $\text{O}_2, \text{SO}_2$ |
| <b>c.</b> $\text{H}_2, \text{O}_2$ | <b>d.</b> $\text{O}_2, \text{Na}$   |

16. If a current of 80.0 microampere is drawn from a cell for 100 days, then the number of faradays involved is

- |                                  |                                 |
|----------------------------------|---------------------------------|
| <b>a.</b> $7.16 \times 10^{-4}$  | <b>b.</b> $7.16 \times 10^{-3}$ |
| <b>c.</b> $14.32 \times 10^{-3}$ | <b>d.</b> $3.46 \times 10^{-3}$ |

17. Specific conductance of 0.01 N solution of an electrolyte is 0.00419 mho  $\text{cm}^{-1}$ . The equivalent conductance of this solution will be:

- |                                    |
|------------------------------------|
| <b>a.</b> 4.19 mho $\text{cm}^2$   |
| <b>b.</b> 419 mho $\text{cm}^2$    |
| <b>c.</b> 0.0419 mho $\text{cm}^2$ |
| <b>d.</b> 0.209 mho $\text{cm}^2$  |

18. The oxidation state of oxygen in  $\text{O}_2\text{PtF}_6$  is

- |                          |                          |
|--------------------------|--------------------------|
| <b>a.</b> zero           | <b>b.</b> $-\frac{1}{2}$ |
| <b>c.</b> $+\frac{1}{2}$ | <b>d.</b> +1             |

19. In the reaction,



**a.** bromine is oxidized and carbonate is reduced

**b.** bromine is reduced and water is oxidized

**c.** bromine is neither reduced nor oxidized

**d.** bromine is both reduced and oxidized.

20. A dilute aqueous solution of  $\text{Na}_2\text{SO}_4$  is electrolyzed using platinum electrodes. The product at the anode and cathode are

- |                                    |                                                   |
|------------------------------------|---------------------------------------------------|
| <b>a.</b> $\text{O}_2, \text{H}_2$ | <b>b.</b> $\text{S}_2\text{O}_8^{2-}, \text{Na}$  |
| <b>c.</b> $\text{O}_2, \text{Na}$  | <b>d.</b> $\text{S}_2\text{O}_8^{2-}, \text{H}_2$ |

21. One mole of a metal ion carries two Faradays of electricity. In the ground state ten orbitals are occupied by electron in the metal ion. The spin only magnetic moment of the metal ion and its atomic number will be respectively, equal to

- |                          |
|--------------------------|
| <b>a.</b> 1.73 BM and 21 |
| <b>b.</b> 1.73 BM and 19 |
| <b>c.</b> 0.0 BM and 20  |
| <b>d.</b> 2.82 BM and 21 |

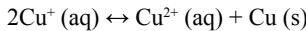
22. The specific conductance of 0.1 N KCl solution at 23°C is  $0.012 \text{ ohm}^{-1} \text{ cm}^{-1}$ . The resistance of cell containing the solution at the same temperature was found to be 55 ohm. The cell constant will be

- |                                   |                                   |
|-----------------------------------|-----------------------------------|
| <b>a.</b> $0.142 \text{ cm}^{-1}$ | <b>b.</b> $0.616 \text{ cm}^{-1}$ |
| <b>c.</b> $6.16 \text{ cm}^{-1}$  | <b>d.</b> $616 \text{ cm}^{-1}$   |

23. The equivalent conductance of  $\text{Ba}^{2+}$  and  $\text{Cl}^-$  are respectively 127 and 76  $\text{ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$  at infinite dilution. The equivalent conductance (in  $\text{ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ ) of  $\text{BaCl}_2$  at infinite dilution will be

- |                 |                 |
|-----------------|-----------------|
| <b>a.</b> 139.5 | <b>b.</b> 203   |
| <b>c.</b> 279   | <b>d.</b> 101.5 |

24.  $\text{Cu}^+$  (aq) is unstable in solution and undergoes simultaneous oxidation and reduction according to the reaction,



choose correct  $E^\circ$  for above reaction if:

$$E^\circ \text{ Cu}^{2+}/\text{Cu} = 0.34 \text{ V} \text{ and } E^\circ \text{ Cu}^{2+}/\text{Cu}^+ = 0.15 \text{ V}$$

- |                   |                   |
|-------------------|-------------------|
| <b>a.</b> -0.38 V | <b>b.</b> +0.49 V |
| <b>c.</b> +0.38 V | <b>d.</b> -0.19 V |

25. The electrode potentials of half-cell reactions are:  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ ;  $E = -0.76 \text{ V}$  and  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ ;  $E = 0.41 \text{ V}$ . The emf of the cell  $\text{Fe}^{2+} + \text{Zn} \rightarrow \text{Zn}^{2+} + \text{Fe}$  is

- |                   |                   |
|-------------------|-------------------|
| <b>a.</b> +0.35 V | <b>b.</b> -1.17 V |
| <b>c.</b> -0.35 V | <b>d.</b> +1.17 V |

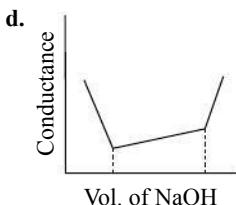


- 38.** Same amount of electric current is passed through solutions of  $\text{AgNO}_3$  and  $\text{HCl}$ . If 1.08 g of silver is obtained in the first case, the volume of hydrogen liberated at STP in the second case is
- 224 ml
  - 112 ml
  - 1120 ml
  - 2240 ml
- 39.** The e.m.f. of a Daniell cell at 298 K is  $E_1$
- $$\text{Zn} | \text{ZnSO}_4 \parallel \text{CuSO}_4 | \text{Cu}$$
- $$(0.01 \text{ M}) \quad (1.0 \text{ M})$$
- when the concentration of  $\text{ZnSO}_4$  is 1.0 M and that of  $\text{CuSO}_4$  is 0.01M, the e.m.f. changed to  $E_2$ . What is the relationship between  $E_1$  and  $E_2$ ?
- $E_1 = E_2$
  - $E_2 = 0 \neq E_1$
  - $E_1 > E_2$
  - $E_1 < E_2$
- 40.** A galvanic cell is constructed using the redox reaction
- $$\frac{1}{2} \text{H}_2(\text{g}) + \text{AgCl}(\text{s}) \leftrightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Ag}(\text{s}).$$
- It is represented as
- Pt |  $\text{H}_2(\text{g}) | \text{HCl}(\text{soln}) \parallel \text{AgNO}_3(\text{soln}) | \text{Ag}$
  - $\text{Ag} | \text{AgCl}(\text{s}) | \text{KCl}(\text{soln}) \parallel \text{HCl}(\text{soln}), \text{H}_2 | \text{Pt}$
  - Pt |  $\text{H}_2(\text{g}) | \text{HCl}(\text{soln}) \parallel \text{AgCl}(\text{s}) | \text{Ag}$
  - Pt |  $\text{H}_2(\text{g}) | \text{KCl}(\text{soln}) \parallel \text{AgCl}(\text{s}) | \text{Ag}$
- 41.** The standard electrode potential for the reaction  $\text{Zn} + \text{Cu}^{2+} \leftrightarrow \text{Cu} + \text{Zn}^{2+}$  is 1.1 V. The electrode potential for the reaction, when 0.1 M  $\text{Cu}^{2+}$  and 0.1 M  $\text{Zn}^{2+}$  solution is used, will be
- 1.1 V
  - 0.11 V
  - 11.0 V
  - +0.011 V
- 42.** For the redox reaction
- $$\text{Zn}(\text{s}) + \text{Cu}^{2+}(0.1 \text{ M}) \rightarrow \text{Zn}^{2+}(1\text{M}) + \text{Cu}(\text{s})$$
- Taking place in a cell,  $E^\circ_{\text{cell}}$  is 1.10 volt.  $E_{\text{cell}}$  for the cell will be ( $2.303 \text{ RT/F} = 0.0591$ )
- 2.14 V
  - 1.80 V
  - 1.07 V
  - 0.82 V
- 43.** For a cell reaction involving a two electron, the standard EMF of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction at 25°C will be
- $1 \times 10^{-10}$
  - $29.5 \times 10^{-2}$
  - 10
  - $1 \times 10^{10}$
- 44.**  $\text{Zn}(\text{s}) + \text{Cl}_2(1 \text{ atm}) \rightarrow \text{Zn}^{2+} + 2\text{Cl}^-$
- The  $E^\circ$  of the cell is 2.12 V. To increase  $E$
- a.**  $\text{Cl}^-$  concentration should be increased  
**b.** Partial pressure of  $\text{Cl}_2$  should be decreased  
**c.**  $\text{Zn}^{2+}$  concentration should be increased  
**d.**  $\text{Zn}^{2+}$  concentration should be decreased
- 45.**  $\text{Cr}_2\text{O}_7^{2-} + \text{I}^- \rightarrow \text{I}_2 + \text{Cr}^{3+}$
- $$E^\circ_{\text{cell}} = 0.79 \text{ V}, E^\circ_{\text{Cr}_2\text{O}_7^{2-}} = 1.33 \text{ V}$$
- $$E^\circ_{\text{I}_2} = ?$$
- +0.18 V
  - 0.18 V
  - 0.54 V
  - 0.054 V
- 46.** An electric current is passed through silver voltameter connected to a water voltameter. The cathode of the silver voltameter weighed 0.108 g more at the end of the electrolysis. The volume of oxygen evolved at STP is
- 5.6 cm<sup>3</sup>
  - 56 cm<sup>3</sup>
  - 11.2 cm<sup>3</sup>
  - 560 cm<sup>3</sup>
  - 22.4 cm<sup>3</sup>
- 47.** Ionic mobility of  $\text{Ag}^+$  is ( $\lambda_{\text{Ag}^+} = 5 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$ )
- $2.6 \times 10^{-9}$
  - $5.2 \times 10^{-9}$
  - $1.54 \times 10^{-9}$
  - $8.46 \times 10^{-9}$
- 48.** The limiting molar conductivities  $\Lambda^\circ$  for  $\text{NaCl}$ ,  $\text{KBr}$  and  $\text{KCl}$  are 126, 152 and 150 S cm<sup>2</sup> mol<sup>-1</sup> respectively. The  $\Lambda^\circ$  for  $\text{NaBr}$  is
- 278 S cm<sup>2</sup> mol<sup>-1</sup>
  - 178 S cm<sup>2</sup> mol<sup>-1</sup>
  - 128 S cm<sup>2</sup> mol<sup>-1</sup>
  - 306 S cm<sup>2</sup> mol<sup>-1</sup>
- 49.** In a cell that utilizes the reaction
- $$\text{Zn}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$$
- Addition of  $\text{H}_2\text{SO}_4$  to cathode compartment, will
- lower the E and shift equilibrium to the right
  - lower the E and shift the equilibrium to the left
  - increase the E and shift the equilibrium to the left
  - increase the E and shift the equilibrium to the right.
- 50.** The  $E_{\text{M}^{3+}/\text{M}^{2+}}$  values for Cr, Mn, Fe and Co are -0.41, +1.57, +0.77 and +1.97 V respectively. For which one of these metals the change in oxidation state from +2 to +3 is easiest?
- Cr
  - Mn
  - Fe
  - Co

## 6.34 ■ Electrochemistry

51. The hydrogen electrode is dipped in a solution of pH 3 at 25°C. The potential would be (the value of  $2.303 RT / F$  is 0.059 V)
- 0.177 V
  - 0.087 V
  - 0.059 V
  - 0.177 V.
52. Corrosion of iron is essentially an electrochemical phenomenon where the cell reactions are
- Fe is oxidized to  $\text{Fe}^{2+}$  and dissolved oxygen in water is reduced to  $\text{OH}^-$
  - Fe is oxidized to  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}$  is reduced to  $\text{O}_2^{2-}$
  - Fe is oxidized to  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}$  is reduced to  $\text{O}_2^-$
  - Fe is oxidized to  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}$  is reduced to  $\text{O}_2$ .
53. Aluminium oxide may be electrolyzed at 1000°C to furnish aluminium metal (atomic mass = 27 amu; 1 faraday = 965000 coulombs). The cathode reaction is
- $$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}^0$$
- To prepare 5.12 kg of aluminium metal by this method would require
- $5.49 \times 10^7$  C of electricity
  - $1.83 \times 10^7$  C of electricity
  - $5.49 \times 10^4$  C of electricity
  - $5.49 \times 10^{10}$  C of electricity
54. Electrolyte KCl KNO<sub>3</sub> HCl NaOAc NaCl  
 $(S \text{ cm}^2 \quad 149.9 \quad 145 \quad 426.2 \quad 91.0 \quad 126.5 \text{ mol}^{-1})$
- Calculate using appropriate molar conductances of the electrolytes listed above at infinite dilution in  $\text{H}_2\text{O}$  at 25°C .
- 517.2
  - 552.7
  - 390.7
  - 217.5
55. The chemical reaction,  
 $2\text{AgCl}(\text{s}) + \text{H}_2(\text{g}) \rightarrow 2\text{HCl}(\text{aq}) + 2\text{Ag}(\text{s})$   
taking place in a galvanic cell is represented by the notation
- Pt(s) |  $\text{H}_2(\text{g}), 1 \text{ bar} | 1 \text{ M KCl}(\text{aq}) | \text{AgCl}(\text{s}) | \text{Ag}(\text{s})$
  - Pt(s) |  $\text{H}_2(\text{g}), 1 \text{ bar} | 1 \text{ M KCl}(\text{aq}) | 1 \text{ M Ag}^+(\text{aq}) | \text{Ag}(\text{s})$
  - Pt(s) |  $\text{H}_2(\text{g}), 1 \text{ bar} | 1 \text{ M KCl}(\text{aq}) | \text{AgCl}(\text{s}) | \text{Ag}(\text{s})$
  - Pt(s) |  $\text{H}_2(\text{g}), 1 \text{ bar} | 1 \text{ M KCl}(\text{aq}) | \text{Ag}(\text{s}) | \text{AgCl}(\text{s})$

56. The number of moles of  $\text{KMnO}_4$  reduced by one mole of KI in alkaline medium is
- 2
  - 1
  - 5
  - 6
57. A hypothetical electrochemical cell is shown below
- $$\text{A}^\ominus | \text{A}^+(\text{xM}) \parallel \text{B}^+(\text{yM}) | \text{B}^\oplus$$
- The emf measured is +0.20 V. the cell reaction is
- the cell reaction cannot be predicted
  - $\text{A} + \text{B}^+ \rightarrow \text{A}^+ + \text{B}$
  - $\text{A}^+ + \text{B} \rightarrow \text{A} + \text{B}^+$
  - $\text{A}^+ + \text{e}^- \rightarrow \text{A}; \quad \text{B}^+ + \text{e}^- \rightarrow \text{B}$
58. If  $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.441 \text{ V}$  and  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.771 \text{ V}$ , the standard EMF of the reaction
- $$\text{Fe} + 2\text{Fe}^{3+} \rightarrow 3\text{Fe}^{2+}$$
- will be
- 1.212 V
  - 0.111 V
  - 0.330 V
  - 1.653 V
59. If equivalent conductance of 1 M benzoic acid is  $12.8 \text{ ohm}^{-1} \text{ cm}^2$  and if the conductance of benzoate ion and  $\text{H}^+$  ion are 42 and  $288.42 \text{ ohm}^{-1} \text{ cm}^2$  respectively, its degree of dissociation is
- 3.9 %
  - 0.039 %
  - 39 %
  - 0.34 %
60. Conductometric titration curve of an equimolar mixture of a HCl and HCN with NaOH(aq) can be given as
- a.
- 
- b.
- 
- c.
-



**61.** Two electrochemical cell

$\text{Zn} | \text{Zn}^{2+} \parallel \text{Cu}^{2+} | \text{Cu}$  and  $\text{Fe} | \text{Fe}^{2+} \parallel \text{Cu}^{2+} | \text{Cu}$  are connected in series. What will be the net e.m.f. of the cell at  $25^\circ\text{C}$ ?

Given:  $\text{Zn}^{2+} | \text{Zn} = -0.73 \text{ V}$ ,

$\text{Cu}^{2+} | \text{Cu} = +0.34 \text{ V}$

$\text{Fe}^{2+} | \text{Fe} = -0.41 \text{ V}$

- a. +1.85
- b. -1.85 V
- c. +0.83 V
- d. -0.83 V

**62.** The reaction potential values of M, N and O are  $+2.46, -1.13$  and  $-3.13 \text{ V}$  respectively. Which of the following order is correct regarding their reducing property?

- a. O > N > M
- b. O > M > N
- c. M > N > O
- d. M > O > N

**63.** If the aqueous solutions of the following salts are electrolyzed for 1 hour with 10 ampere current, which solution will deposit the maximum mass of the metal at the cathode? The atomic weights are, Fe = 56, Zn = 65, Ag = 108, Hf = 178 and W = 184

- a.  $\text{ZnSO}_4$
- b.  $\text{FeCl}_3$
- c.  $\text{WCl}_6$
- d.  $\text{AgNO}_3$

**64.** Given the standard reduction potentials  $\text{Zn}^{2+} / \text{Zn} = -0.74 \text{ V}$ ,  $\text{Cl}_2 / \text{Cl}^- = 1.36 \text{ V}$ ,  $\text{H}^+ / \frac{1}{2}\text{H}_2 = 0 \text{ V}$  and  $\text{Fe}^{2+} / \text{Fe}^{3+} = \text{V}$ . The order of increasing strength as reducing agent is

- a.  $\text{Zn}, \text{H}_2, \text{Fe}^{2+}, \text{Cl}^-$
- b.  $\text{H}_2, \text{Zn}, \text{Fe}^{2+}, \text{Cl}^-$
- c.  $\text{Cl}^-, \text{Fe}^{2+}, \text{H}_2, \text{Zn}$
- d.  $\text{Cl}^-, \text{Fe}^{2+}, \text{Zn}, \text{H}_2$

**65.** Given the data at  $25^\circ\text{C}$

$\text{Ag} + \text{I}^- \rightarrow \text{AgI} + \text{e}^- ; E^\circ = 0.152 \text{ V}$

$\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^- ; E^\circ = -0.800 \text{ V}$

What is the value of  $\log K_{\text{sp}}$  for  $\text{AgI}$ ?

$(2.303 \text{ RT/F} = 0.059 \text{ V})$

- a. -8.12
- b. +8.612
- c. -37.83
- d. -16.13

**66.** One mole of acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  on reaction with excess  $\text{KI}$  will liberate ..... moles of  $\text{I}_2$

- a. 1
- b. 2
- c. 3
- d. 5
- e. 7

**67.** The products formed when an aqueous solution of  $\text{NaBr}$  is electrolyzed in a cell having inert electrodes are

- a.  $\text{Na}$  and  $\text{Br}_2$
- b.  $\text{Na}$  and  $\text{O}_2$
- c.  $\text{H}_2, \text{Br}_2$  and  $\text{NaOH}$
- d.  $\text{H}_2$  and  $\text{O}_2$

**68.** The charge required for the reduction of 1 mol of  $\text{MnO}_4^-$  to  $\text{MnO}_2$  is

- a. 1 F
- b. 3 F
- c. 5 F
- d. 6 F

**69.** What current is to be passed for 0.25 s for deposition of a certain weight of metal which is equal to its electrochemical equivalent?

- a. 2 A
- b. 4 A
- c. 100 A
- d. 200 A

**70.** If the molar conductance values of  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  at infinite dilution are respectively,  $118.88 \times 10^{-4} \text{ m}^2 \text{ mho mol}^{-1}$  and  $77.33 \times 10^{-4} \text{ m}^2 \text{ mho mol}^{-1}$ , then that of  $\text{CaCl}_2$  is ( $\text{m}^2 \text{ mho mol}^{-1}$ )

- a.  $153.56 \times 10^{-4}$
- b.  $273.54 \times 10^{-4}$
- c.  $183.24 \times 10^{-4}$
- d.  $196.84 \times 10^{-4}$

**71.**  $\text{Ag} (\text{s}) | \text{Ag}^+ (\text{aq}) (0.01 \text{ M}) \parallel \text{Ag}^+ (\text{aq}) (0.1 \text{ M}) | \text{Ag} (\text{s}), E^\circ_{\text{Ag}} (\text{s}) / \text{Ag}^+ (\text{aq}) = 0.80 \text{ Volt}$

- a.  $E_{\text{cell}} = 0.80 \text{ V}$
- b.  $E_{\text{cell}} = 0.0296 \text{ V}$
- c.  $E_{\text{cell}} = 0.0591 \text{ V}$
- d. Cell cannot function as anode and cathode are of the same material

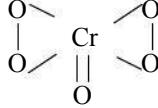
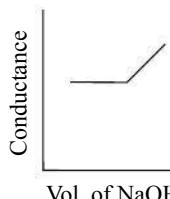
**72.** Find the equivalent weight of  $\text{Cr}_2\text{O}_7^{2-}$  in the following reaction:

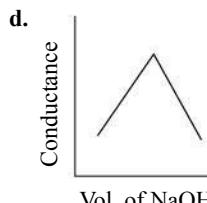
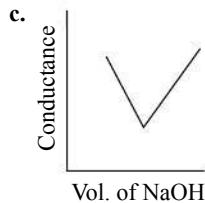
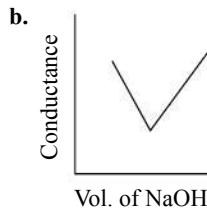


- a. Molecular weight / 2
- b. Molecular weight / 3
- c. Molecular weight / 4
- d. Molecular weight / 6

**73.**  $\text{KMnO}_4$  is a strong oxidizing agent in acid medium. To provide acid medium  $\text{H}_2\text{SO}_4$  is used instead of  $\text{HCl}$ . This is because

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- a. Only  $\text{H}_2\text{SO}_4$  is completely ionized.  
 b. Rate is faster in the presence of  $\text{H}_2\text{SO}_4$   
 c.  $\text{H}_2\text{SO}_4$  is a dibasic acid  
 d. HCl is oxidized by  $\text{KMnO}_4$  to  $\text{Cl}_2$   
 e.  $\text{H}_2\text{SO}_4$  is a stronger acid than HCl.
74.  $\text{Zn}^{2+} \rightarrow \text{Zn(s)}; E^\circ = -0.76 \text{ V}$   
 $\text{Cu}^{2+} \rightarrow \text{Cu(s)}; E^\circ = -0.34 \text{ V}$
- Which of the following is spontaneous?
- a.  $\text{Zn}^{2+} + \text{Cu} \rightarrow \text{Zn} + \text{Cu}^{2+}$   
 b.  $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$   
 c.  $\text{Zn}^{2+} + \text{Cu}^{2+} \rightarrow \text{Zn} + \text{Cu}$   
 d. None of the above
75. The standard e.m.f. of a galvanic cell involving cell reaction with  $n = 2$  is found to be 0.295 V at 25°C. The equilibrium constant of the reaction would be  
 (Given  $F = 96500 \text{ C mol}^{-1}$ ;  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ )
- a.  $2.0 \times 10^{11}$       b.  $4.0 \times 10^{12}$   
 c.  $1.0 \times 10^2$       d.  $1.0 \times 10^{10}$
76. Oxidation state of chromium in
- 
- a. +9      b. +6  
 c. +1      d. -4
77. The standard potential of the half cell reaction  $\text{Zn}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Zn}(\text{s})$  is -0.7628 V at 25°C  
 The standard potential for the reaction,  
 $2\text{Zn}^{2+} + 4e^- \rightarrow 2\text{Zn}(\text{s})$  is
- a. +0.7628 V      b. -0.7628 V  
 c. -0.3814 V      d. 0.3814 V
78. A dilute solution of  $\text{H}_2\text{SO}_4$  was electrolyzed by passing a current of 2 amp. The time required for formation of 0.5 mole of oxygen is
- a. 13.4 hours      b. 26.8 hours  
 c. 2.68 hours      d. 53.4 hours
79.  $\text{CH}_3\text{COOH}$  can be neutralized by  $\text{NaOH}$ . Conductometric titration curve can be given as
- a. 



80.  $K_{sp}$  of  $\text{BaSO}_4$  is  $1 \times 10^{-10}$ . If the ionic conductances of  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$  ions are 64 and 80  $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  respectively, then its specific conductance is
- a.  $1.44 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$   
 b.  $144 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$   
 c.  $1.44 \times 10^8 \text{ ohm}^{-1} \text{ cm}^{-1}$   
 d.  $144 \times 10^8 \text{ ohm}^{-1} \text{ cm}^{-1}$

### Brainteasers Objective Type Questions (Single choice only)

81. The e.m.f of the following three galvanic cells:  
 (1)  $\text{Zn} | \text{Zn}^{2+}(1 \text{ M}) \parallel \text{Cu}^{2+}(1 \text{ M}) | \text{Cu}$   
 (2)  $\text{Zn} | \text{Zn}^{2+}(0.1 \text{ M}) \parallel \text{Cu}^{2+}(1 \text{ M}) | \text{Cu}$   
 (3)  $\text{Zn} | \text{Zn}^{2+}(1 \text{ M}) \parallel \text{Cu}^{2+}(0.1 \text{ M}) | \text{Cu}$
- are represented by  $E_1$ ,  $E_2$  and  $E_3$ . Which of the following statement is true?
- a.  $E_2 > E_1 > E_3$       b.  $E_3 > E_2 > E_1$   
 c.  $E_1 > E_2 > E_3$       d.  $E_3 > E_1 > E_2$
82. When an electric current is passed through acidulated water 112 mL of hydrogen gas at NTP collects at the cathode in 965 seconds. The current passes, in ampere is
- a. 0.1      b. 0.5  
 c. 1.0      d. 2.0

- 83.** The charge required to deposit 40.5 g of Al (atomic mass = 27.0 g) from the fused  $\text{Al}_2(\text{SO}_4)_3$  is  
**a.**  $0.434 \times 10^5 \text{ C}$       **b.**  $4.34 \times 10^5 \text{ C}$   
**c.**  $3.34 \times 10^5 \text{ C}$       **d.**  $43.4 \times 10^5 \text{ C}$
- 84.** The hydrogen electrode is dipped in a solution of pH = 3.0 at 25°C. The potential of hydrogen electrode would be  
**a.** -0.177 V      **b.** 0.177 V  
**c.** 1.77 V      **d.** 0.277 V
- 85.** Three faraday of electricity is passed through aqueous solutions of  $\text{AgNO}_3$ ,  $\text{NiSO}_4$  and  $\text{CrCl}_3$  kept in three vessels using inert electrodes. The ratio in mol in which the metals Ag, Ni and Cr will be deposited is  
**a.** 1 : 2 : 3      **b.** 2 : 3 : 6  
**c.** 6 : 3 : 2      **d.** 3 : 2 : 6
- 86.** Calculate the weight of copper that will be deposited at the cathode in the electrolysis of a 0.2 M solution of copper sulphate when quantity of electricity equal to the required to liberate 2.24 L of hydrogen at STP from a 0.1 M aqueous sulphuric acid, is passed (atomic mass of Cu = 63.5)  
**a.** 6.35 g      **b.** 3.17 g  
**c.** 12.71 g      **d.** 63.5 g
- 87.** The same amount of electricity was passed through two separate electrolytic cells containing solutions of nickel nitrate and chromium nitrate respectively. If 0.3 g of nickel was deposited in the first cell, the amount of chromium deposited is (atomic weight of Ni = 59, Cr = 52)  
**a.** 0.130 g      **b.** 0.236 g  
**c.** 0.176 g      **d.** 1.76 g
- 88.** Given that:  $E^\circ (\text{Zn}^{2+} / \text{Zn}) = -0.763 \text{ V}$  and  $E^\circ (\text{Cd}^{2+} / \text{Cd}) = -0.403 \text{ V}$ , the emf of the following cell:  
 $\text{Zn} | \text{Zn}^{2+} (\text{a} = 0.04) \parallel \text{Cd}^{2+} (\text{a} = 0.2) | \text{Cd}$   
is given by  
**a.**  $E = +0.36 + [0.059 / 2] [\log (0.2/0.004)]$   
**b.**  $E = -0.36 + [0.059 / 2] [\log (0.2/0.004)]$   
**c.**  $E = +0.36 + [0.059 / 2] [\log (0.004/0.2)]$   
**d.**  $E = -0.36 + [0.059 / 2] [\log (0.004/0.2)]$
- 89.** If the pressure of hydrogen gas is increased from 1 atm to 100 atm, keeping the hydrogen ion concentration constant at 1 M, the voltage of the hydrogen half cell at 25°C will be  
**a.** -0.059 V      **b.** +0.059 V  
**c.** 5.09 V      **d.** 0.259 V
- 90.** When a current of 1.5 ampere is passed through acidulated water for two hours, then volume of hydrogen ( $\text{H}_2$ ) at NTP produced will be  
**a.** 1.5 litre      **b.** 0.5 litre  
**c.** 1.25 litre      **d.** 2.5 litre
- 91.** For the following cell with hydrogen electrodes at two different pressures  $p_1$  and  $p_2$   
 $\text{Pt}(\text{H}_2) | \text{H}^+(\text{aq}) | \text{Pt}(\text{H}_2)$   
 $p_1 \qquad \qquad \qquad 1\text{M} \qquad \qquad p_2$   
EMF is given by  
**a.**  $RT/F \log_e p_1 / p_2$   
**b.**  $RT/2F \log_e p_1 / p_2$   
**c.**  $RT/F \log_e p_2 / p_1$   
**d.**  $RT/2F \log_e p_2 / p_1$
- 92.** Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100  $\Omega$ . The conductivity of this solution is  $1.29 \text{ S m}^{-1}$ . Resistance of the same cell when filled with 0.2 M of the same solution is 520  $\Omega$ . The molar conductivity of 0.02 M solution of the electrolyte will be  
**a.**  $124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$   
**b.**  $1240 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$   
**c.**  $1.24 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$   
**d.**  $12.4 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
- 93.** Which of the following reactions is most suitable for a fuel cell?  
**a.**  $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$   
**b.**  $\text{MnO}_2(\text{s}) + \text{Li}(\text{s}) \rightarrow \text{LiMnO}_2(\text{s})$   
**c.**  $\text{HgO}(\text{l}) + \text{Zn}(\text{s}) \rightarrow \text{ZnO}(\text{s}) + \text{Hg}(\text{l})$   
**d.**  $\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{H}^+(\text{aq}) + \text{HSO}_4^-(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$
- 94.** The volume of  $\text{H}_2$  gas at NTP obtained by passing 4 amperes through acidified  $\text{H}_2\text{O}$  for 30 minutes is  
**a.** 0.187 L      **b.** 0.836 L  
**c.** 0.0836 L      **d.** 0.0536 L
- 95.**  $a\text{K}_2\text{Cr}_2\text{O}_7 + b\text{KCl} + c\text{H}_2\text{SO}_4 \rightarrow x\text{CrO}_2\text{Cl}_2 + y\text{KHSO}_4 + z\text{H}_2\text{O}$   
The above equation balances when  
**a.**  $a = 1, b = 6, c = 4$  and  $x = 6, y = 2, z = 3$   
**b.**  $a = 2, b = 4, c = 6$  and  $x = 2, y = 6, z = 3$

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- c.  $a = 1, b = 4, c = 6$  and  $x = 2, y = 6, z = 3$   
 d.  $a = 4, b = 2, c = 6$  and  $x = 6, y = 2, z = 3$   
 e.  $a = 6, b = 4, c = 2$  and  $x = 6, y = 3, z = 2$
96. The standard emf of the cell  
 $\text{Cd (s)} | \text{CdCl}_2 (0.1 \text{ M}) \parallel \text{AgCl (s)} | \text{Ag (s)}$  in which the cell reaction is  
 $\text{Cd (s)} + 2\text{AgCl (s)} \rightarrow 2\text{Ag (s)} + \text{Cd}^{2+} (\text{aq}) + 2\text{Cl}^- (\text{aq})$   
 is  $0.6915 \text{ V}$  at  $0^\circ\text{C}$  and  $0.6753 \text{ V}$  at  $25^\circ\text{C}$ ,  
 The enthalpy change of the reaction at  $25^\circ\text{C}$  is  
 a.  $-346.8 \text{ kJ}$       b.  $-176.0 \text{ kJ}$   
 c.  $-167.6 \text{ kJ}$       d.  $+127.6 \text{ kJ}$
97.  $4.5 \text{ g}$  of aluminium (at. mass  $27 \text{ amu}$ ) is deposited at cathode from  $\text{Al}^{3+}$  solution by a certain quantity of electric charge. The volume of hydrogen produced at STP from  $\text{H}^+$  ions in solution by the same quantity of electric charge will be  
 a.  $44.8 \text{ L}$       b.  $22.4 \text{ L}$   
 c.  $11.2 \text{ L}$       d.  $5.6 \text{ L}$ .
98. If  $\text{Zn}^{2+} / \text{Zn}$  electrode is diluted 100 times, then the change in emf is  
 a. Decrease of  $29.5 \text{ mV}$   
 b. Increase of  $29.5 \text{ mV}$   
 c. Decrease of  $59 \text{ mV}$   
 d. Increase of  $59 \text{ mV}$
99. Two electrochemical cells,  
 $\text{Zn} | \text{Zn}^{2+} \parallel \text{Cu}^{2+} | \text{Cu}$  and  
 $\text{Fe} | \text{Fe}^{2+} \parallel \text{Cu}^{2+} | \text{Cu}$   
 are connected in series. What will be the net e.m.f. of the cell at  $25^\circ\text{C}$ ?  
 Given:  $\text{Zn}^{2+} | \text{Zn} = -0.76 \text{ V}$ ,  
 $\text{Cu}^{2+} | \text{Cu} = +0.34 \text{ V}$ ,  
 $\text{Fe}^{2+} | \text{Fe} = -0.41 \text{ V}$   
 a.  $-1.85 \text{ V}$       b.  $-0.83 \text{ V}$   
 c.  $+0.83 \text{ V}$       d.  $+1.85 \text{ V}$
100. In the reaction,  
 $\text{As}_2\text{S}_3 + x\text{HNO}_3 \rightarrow 5\text{H}_2\text{SO}_4 + y\text{NO}_2 + 2\text{H}_3\text{AsO}_4 + 12\text{H}_2\text{O}$ ,  
 The values of  $x$  and  $y$  are  
 a.  $30, 30$       b.  $40, 40$   
 c.  $10, 10$       d.  $20, 20$

101. Given that  $E^\circ = +0.897 \text{ V}$ ,  
 $\text{Pb (s)} | \text{Pb}^{2+} (0.040 \text{ M}) \parallel \text{Fe}^{3+} (0.20 \text{ M}), \text{Fe}^{2+} (0.010 \text{ M}) | \text{Pt (s)}$   
 Calculate  $E$  at  $25^\circ\text{C}$ .  
 a.  $+1.139 \text{ V}$       b.  $+1.015 \text{ V}$   
 c.  $+0.669 \text{ V}$       d.  $+0.926 \text{ V}$
102. The equilibrium constant of the reaction:  
 $\text{Cu (s)} + 2\text{Ag}^+ (\text{aq}) \rightarrow \text{Cu}^{2+} (\text{aq}) + 2\text{Ag (s)}$ ;  
 $E^\circ = 0.46 \text{ V}$  at  $298 \text{ K}$  is  
 a.  $2.4 \times 10^{10}$       b.  $2.0 \times 10^{10}$   
 c.  $4.0 \times 10^{10}$       d.  $4.0 \times 10^{15}$
103. The standard oxidation potentials of Zn, Cu, Ag and Ni electrodes are  $+0.76, -0.34, -0.80$  and  $+0.25 \text{ V}$  respectively. Which of the following reaction will provide maximum voltage?  
 a.  $\text{Zn} + 2\text{Ag}^+ (\text{aq}) \rightarrow \text{Zn}^{2+} (\text{aq}) + 2\text{Ag}$   
 b.  $\text{Cu} + 2\text{Ag}^+ (\text{aq}) \rightarrow \text{Cu}^{2+} (\text{aq}) + 2\text{Ag}$   
 c.  $\text{Zn} + 2\text{H}^+ (\text{aq}) \rightarrow \text{Zn}^{2+} (\text{aq}) + \text{H}_2$   
 d.  $\text{Zn} + \text{Cu}^{2+} (\text{aq}) \rightarrow \text{Zn}^{2+} (\text{aq}) + \text{Cu}$
104. The reduction potential of a half cell consisting of a Pt electrode immersed in  $1.2 \text{ M}$   $\text{Fe}^{2+}$  and  $0.012 \text{ M}$   $\text{Fe}^{3+}$  solution at  $25^\circ\text{C}$  is ( $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.770$ )  
 a.  $-0.326 \text{ V}$       b.  $0.652 \text{ V}$   
 c.  $0.326 \text{ V}$       d.  $-0.652 \text{ V}$
105. The standard potentials of  $\text{OCl}^- / \text{Cl}^-$  and  $\text{Cl}^- / \frac{1}{2} \text{Cl}_2$  are  $0.94 \text{ V}$  and  $1.36 \text{ V}$  respectively. The  $E^\circ$  value of  $\text{OCl}^- / \frac{1}{2} \text{Cl}_2$  will be  
 a.  $-0.42 \text{ V}$       b.  $2.3 \text{ V}$   
 c.  $0.42 \text{ V}$       d.  $0.0 \text{ V}$
106. The cell  $\text{Zn} | \text{Zn}^{2+} (1 \text{ M}) \parallel \text{Cu}^{2+} (1 \text{ M}) | \text{Cu}$  ( $E^\circ_{\text{cell}} = 1.10 \text{ V}$ ), was allowed to be completely discharged at  $298 \text{ K}$ . The relative concentration of  $\text{Zn}^{2+}$  to  $\text{Cu}^{2+}$  ( $[\text{Zn}^{2+}] / [\text{Cu}^{2+}]$ ) is  
 a.  $37.3$       b.  $10^{37.3}$   
 c.  $9.65 \times 10^4$       d. antilog (24.08)
107. In an experiment  $0.04 \text{ F}$  was passed through  $400 \text{ ml}$  of a  $1 \text{ M}$  solution of  $\text{NaCl}$ . What would be the pH of the solution after the electrolysis?  
 a. 8      b. 10  
 c. 12      d. 13
108. The resistance of N/10 solution is found to be  $2.5 \times 10^3 \text{ ohms}$ . The equivalent conductance of the solution is (cell constant =  $1.25 \text{ cm}^{-1}$ )  
 a.  $1.25 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ .  
 b.  $5.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ .

- c.  $2.5 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ equiv}^{-1}$ .  
 d.  $2.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ .  
 e.  $5.5 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ equiv}^{-1}$ .
- 109.** How long (in hours) must a current of 5.0 amperes be maintained to electroplate 60 g of calcium from molten  $\text{CaCl}_2$ ?  
 a. 16 hours      b. 11 hours  
 c. 8.6 hours      d. 26 hours
- 110.** An alloy of Pb-Ag weighing 1.08 g was dissolved in dilute  $\text{HNO}_3$  and the volume made to 100 ml. A silver electrode was dipped in the solution and the EMF of the cell set up  
 $\text{Pt (s), H}_2\text{(g)} | \text{H}^+(\text{1M}) \parallel \text{Ag}^+(\text{aq}) | \text{Ag (s)}$   
 was 0.62 V. If  $E^\circ_{\text{cell}} = 0.80 \text{ V}$ . What is the percentage of Ag in the alloy? [At  $25^\circ\text{C}$ ,  $\text{RT/F} = 0.06$ ]  
 a. 1 %      b. 10 %  
 c. 25 %      d. 50 %  
 e. 75 %
- 111.** Based on the following information,  
 $\text{F}_2\text{(g)} + 2\text{e}^- \rightarrow 2\text{F}^- \text{(aq)} \quad E^\circ = +2.87 \text{ V}$   
 $\text{Mg}^{2+}\text{(aq)} + 2\text{e}^- \rightarrow 2\text{Mg (s)} \quad E^\circ = -2.37 \text{ V}$   
 Which of the following chemical species is the strongest reducing agent?  
 a.  $\text{F}^- \text{(aq)}$       b.  $\text{F}_2 \text{(g)}$   
 c.  $\text{Mg (s)}$       d.  $\text{Mg}^{2+} \text{(aq)}$
- 112.**  $E^\circ \text{Cr}^{3+}/\text{Cr}^{2+} = -0.41 \text{ V}$  The amount of chlorine evolved, when 2A of current is passed for 30 minutes in an aqueous solution of  $\text{NaCl}$  will be  
 a. 1.32 g      b. 3.54 g  
 c. 12.5 g      d. 8.56 g
- 113.** The oxidation states of sulphur in the anions  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_4^{2-}$  and  $\text{S}_2\text{O}_6^{2-}$  follow the order:  
 a.  $\text{SO}_3^{2-} < \text{S}_2\text{O}_4^{2-} < \text{S}_2\text{O}_6^{2-}$   
 b.  $\text{S}_2\text{O}_4^{2-} < \text{SO}_3^{2-} < \text{S}_2\text{O}_6^{2-}$   
 c.  $\text{S}_2\text{O}_4^{2-} < \text{S}_2\text{O}_6^{2-} < \text{SO}_3^{2-}$   
 d.  $\text{S}_2\text{O}_6^{2-} < \text{S}_2\text{O}_4^{2-} < \text{SO}_3^{2-}$
- 114.** In the balanced chemical reaction,  
 $\text{IO}_3^- + \text{aI}^- + \text{bH}^+ \rightarrow \text{cH}_2\text{O} + \text{dI}_2$   
 a, b, c, and d respectively corresponds to:  
 a. 4, 5, 6, 3      b. 3, 6, 5, 3  
 c. 5, 6, 2, 3      d. 5, 6, 3, 3
- 115.** When a quantity of electricity is passed through  $\text{CuSO}_4$  solution, 0.16 g of copper gets deposited. If the same quantity of electricity is passed through acidulated water, then the volume of  $\text{H}_2$  liberated at STP will be (at. wt. of Cu = 64)  
 a.  $4.0 \text{ cm}^3$       b.  $56 \text{ cm}^3$   
 c.  $604 \text{ cm}^3$       d.  $8.0 \text{ cm}^3$
- 116.** For decolorisation of one mole of  $\text{KMnO}_4$  the moles of  $\text{H}_2\text{O}_2$  required is  
 a. 1/2      b. 3/2  
 c. 5/2      d. 7/2
- 117.** The standard reduction potentials of  $\text{Fe}/\text{Fe}^{2+}$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  are  $-0.44 \text{ V}$  and  $0.77 \text{ V}$  respectively. The reduction potential of  $\text{Fe}/\text{Fe}^{3+}$  couple is  
 a.  $0.11 \text{ V}$       b.  $0.037 \text{ V}$   
 c.  $-0.11 \text{ V}$       d.  $-0.037 \text{ V}$
- 118.**  $2\text{Hg} \rightarrow \text{Hg}_2^{2+}, E^\circ = +0.855 \text{ V}$   
 $\text{Hg} \rightarrow \text{Hg}^{2+}, E^\circ = +0.799 \text{ V}$   
 Equilibrium constant for the reaction  
 $\text{Hg} + \text{Hg}^{2+} \rightarrow \text{Hg}_2^{2+}$  at  $27^\circ\text{C}$  is  
 a. 79      b. 89  
 c. 69      d. 82.9
- 119.** On the basis of the following  $E^\circ$  values, the strongest oxidizing agent is:  
 $[\text{Fe}(\text{CN})_6]^{4-} \rightarrow [\text{Fe}(\text{CN})_6]^{3-}, E^\circ = -0.35 \text{ V}$   
 $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-, E^\circ = -0.77 \text{ V}$   
 a.  $\text{Fe}^{3+}$       b.  $[\text{Fe}(\text{CN})_6]^{3-}$   
 c.  $[\text{Fe}(\text{CN})_6]^{4-}$       d.  $\text{Fe}^{2+}$
- 120.** Consider the following standard reduction potentials,  
 $\text{Al}^{3+} \text{(aq)} + 3\text{e}^- \rightarrow \text{Al (s)} \quad E^\circ = -1.66 \text{ V}$   
 $\text{I}_2 \text{(s)} + 2\text{e}^- \rightarrow 2\text{I}^- \text{(aq)} \quad E^\circ = +0.54 \text{ V}$   
 Under standard conditions,  
 a.  $\text{I}^- \text{(aq)}$  is a stronger oxidizing agent than  $\text{Al (s)}$  and  $\text{I}_2 \text{(s)}$  is a stronger reducing agent than  $\text{Al}^{3+} \text{(aq)}$ .  
 b.  $\text{Al (s)}$  is a stronger oxidizing agent than  $\text{I}^- \text{(aq)}$ , and  $\text{Al}^{3+} \text{(aq)}$  is a stronger reducing agent than  $\text{I}_2 \text{(s)}$ .  
 c.  $\text{I}_2 \text{(s)}$  is a stronger oxidizing agent than  $\text{Al}^{3+} \text{(aq)}$ , and  $\text{Al (s)}$  is a stronger reducing agent than  $\text{I}^- \text{(aq)}$ .  
 d.  $\text{Al}^{3+} \text{(aq)}$  is a stronger oxidizing agent than  $\text{I}_2 \text{(s)}$ , and  $\text{I}^- \text{(aq)}$  is a stronger reducing agent than  $\text{Al (s)}$ .
- 121.** In which of the following the oxidation number of oxygen has been arranged in increasing order?

## 6.40 ■ Electrochemistry

- a.  $\text{OF}_2 < \text{O}_3 < \text{KO}_2 < \text{BaO}_2$
- b.  $\text{BaO}_2 < \text{KO}_2 < \text{O}_3 < \text{OF}_2$
- c.  $\text{OF}_2 < \text{KO}_2 < \text{BaO}_2 < \text{O}_3$
- d.  $\text{KO}_2 < \text{OF}_2 < \text{O}_3 < \text{BaO}_2$
- e.  $\text{BaO}_2 < \text{O}_3 < \text{OF}_2 < \text{KO}_2$

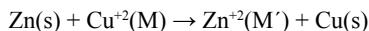
122. If three Faradays of electricity is passed through the solutions of  $\text{AgNO}_3$ ,  $\text{CuSO}_4$  and  $\text{AuCl}_3$ , the molar ratio of the cations deposited at the cathodes will be

- a. 1 : 2 : 3
- b. 6 : 3 : 2
- c. 6 : 1 : 3
- d. 2 : 3 : 1

123. The hydrogen electrode is dipped in a solution of  $\text{pH} = 3$  at  $25^\circ\text{C}$ . The potential of the cell would be (value of  $2.303 \text{ RT/F}$  is 0.059 V)

- a. +1.77 V
- b. +0.177 V
- c. -0.87 V
- d. -0.177 V

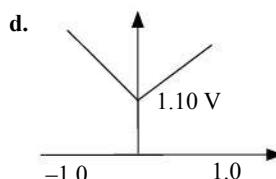
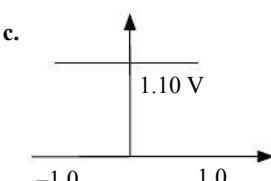
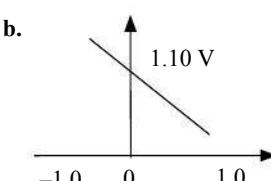
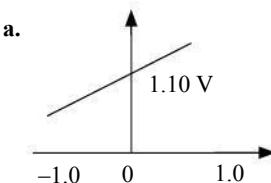
124. Which of these correctly E<sub>cell</sub> as a functions of concentrations for the cell (for different values of M and M')



$$E_{\text{cell}}^{\circ} = 1.10 \text{ V}$$

$$\text{X-axis : } 1 \log 10 \frac{[\text{Zn}^{+2}]}{[\text{Cu}^{+2}]}$$

$$\text{Y-axis: } E_{\text{cell}}$$



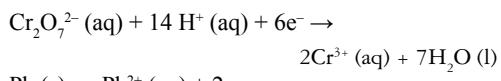
125. What is the relationship between the standard cell potentials  $E^{\circ}$ , for the following two galvanic cell reactions?

- (I)  $2\text{Ag}^{+}(\text{aq}) + \text{Sn}^{2+}(\text{aq}) \rightarrow \text{Sn}^{4+}(\text{aq}) + 2\text{Ag(s)}$
- (II)  $\text{Ag(s)} + \frac{1}{2}\text{Sn}^{4+}(\text{aq}) \rightarrow \frac{1}{2}\text{Sn}^{2+}(\text{aq}) + \text{Ag}^{+}(\text{aq})$
- a.  $E^{\circ} (\text{I}) = 2E^{\circ} (\text{II})$
- b.  $E^{\circ} (\text{I}) = E^{\circ} (\text{II})$
- c.  $E^{\circ} (\text{I}) = -2E^{\circ} (\text{II})$
- d.  $E^{\circ} (\text{I}) = -E^{\circ} (\text{II})$

126. The standard reduction potentials of  $\text{Cu}^{2+}/\text{Cu}$  and  $\text{Cu}^{2+}/\text{Cu}^{+}$  are 0.337 V and 0.153 V respectively. The standard electrode potential of  $\text{Cu}^{+}/\text{Cu}$  half cell is

- a. 0.507 V
- b. 0.421 V
- c. 0.184 V
- d. 0.0501 V

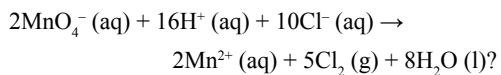
127. For a galvanic cell that uses the following two half reactions,



How many moles of Pb (s) are oxidized by one mole of  $\text{Cr}_2\text{O}_7^{2-}$ ?

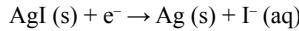
- a. 6
- b. 4
- c. 3
- d. 2

128. How many moles of electrons, are transferred in the following reduction-oxidation reaction?



- a. 2
- b. 5
- c. 10
- d. 12

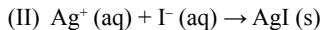
129. Given:



$$E^{\circ} = -0.152 \text{ V}$$

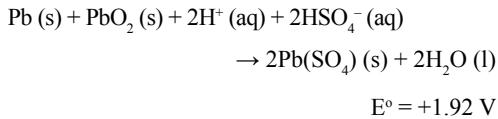


Which of the following reactions should be spontaneous under standard conditions?



- a. I is spontaneous and II is non spontaneous
- b. Both I and II are spontaneous
- c. Both I and II are non spontaneous
- d. I is non-spontaneous and II is spontaneous

130. The cell reaction for a lead storage battery is



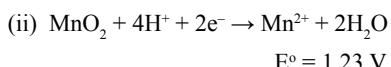
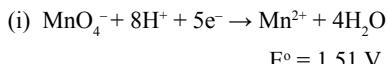
To provide a potential of about 12 V, one could

- a. Connect six cells in series.
- b. Adjust the pH to 12.
- c. Adjust the pH to 1.
- d. Greatly increase the surface area of the Pb (s) and PbO<sub>2</sub> (s).

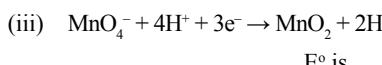
131. If  $E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ V}$  and  $E^\circ_{\text{MnO}_2 / \text{Mn}^{2+}} = 1.23 \text{ V}$ , the  $E^\circ_{\text{MnO}_4^-/\text{MnO}_2}$  is

- a. +1.69 V
- b. -1.69 V
- c. -3.38 V
- d. +0.845 V

132. For the reactions

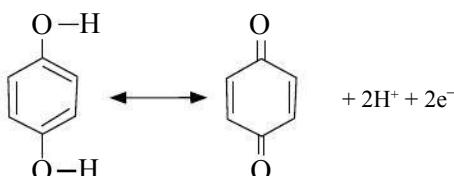


Then for the reaction



- a. 2.45 V
- b. 0.85 V
- c. 1.70 V
- d. -1.70V

133. For the half cell

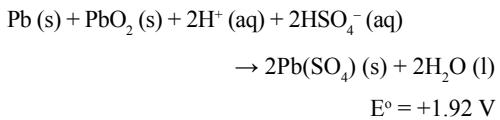


At pH = 2, electrode potential is

- a. 1.36 V
- b. 0.71

- c. 1.42 V
- d. -1.48 V

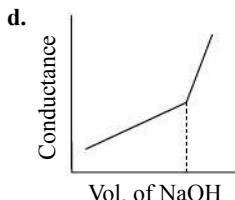
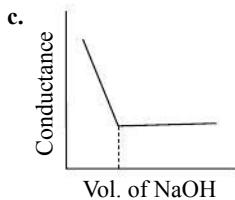
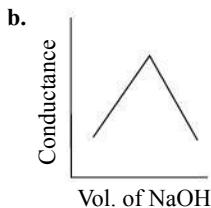
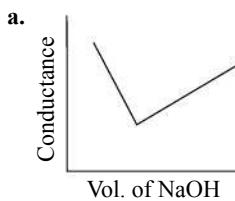
134. The cell reaction for a lead storage battery is



To provide a potential of about 12 V, one could

- a. Connect six cells in series.
- b. Adjust the pH to 12.
- c. Adjust the pH to 1.
- d. Greatly increase the surface area of the Pb (s) and PbO<sub>2</sub> (s).

135. When HNO<sub>3</sub>(aq) is titrated with NaOH (aq) conductometrically, the graphical representation of this titration can be shown as

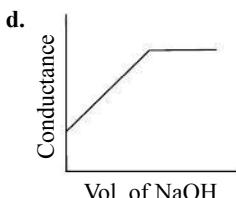
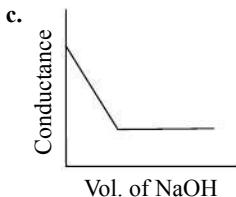


### Multiple Correct Answer Type Questions

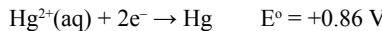
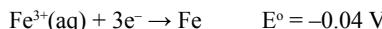
- 136.** Which of the following reaction is/are not possible at anode?
- $\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$
  - $2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{H}_2\text{O}$
  - $2\text{Cr}_2^{3+} + 7\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^-$
  - $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$
- 137.** Which of the following statements are incorrect?
- Specific conductance increases with dilution
  - Equivalent conductance decreases with dilution
  - The conductance of all electrolytes increase with temperature
  - Conductance becomes maximum at infinite dilution.
- 138.** Electrolysis of water gives 11.2 L of hydrogen at STP at the cathode. The oxygen evolved at the anode under similar conditions is
- 5.6 L
  - 11.2 L
  - 0.25 mol
  - 8 g
- 139.** Which of the following statements are correct concerning redox properties?
- A metal M for which  $E^\circ$  for the half reaction  $\text{M}^{n+} + ne \rightleftharpoons \text{M}$  is very negative will be a good reducing agent.
  - The oxidizing power of halogens decreases from chlorine to iodine.
  - The reducing power of hydrogen halides increases from hydrogen chloride to hydrogen iodide.
  - Potassium is a better reductant than lithium.
- 140.** Which of the following statements, about the advantage of roasting of sulphide ore before reduction is/are true?
- Carbon and hydrogen are suitable reducing agents for metal sulphides.
  - The  $\Delta_f G^\circ$  of the sulphide is greater than those for  $\text{CS}_2$  and  $\text{H}_2\text{S}$ .
  - The  $\Delta_f G^\circ$  is negative for roasting of sulphide ore to oxide.
  - Roasting of the sulphide to the oxide is thermodynamically feasible.

- 141.** Which of the following is/are not redox reaction?
- $\text{Zn} + 2\text{AgCN} \rightarrow 2\text{Ag} + \text{Zn}(\text{CN})_2$
  - $\text{Mg}(\text{OH})_2 + 2\text{NH}_4\text{Cl} \rightarrow \text{MgCl}_2 + 2\text{NH}_4\text{OH}$
  - $\text{NaCl} + \text{KNO}_3 \rightarrow \text{NaNO}_3 + \text{KCl}$
  - $\text{CaC}_2\text{O}_4 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{C}_2\text{O}_4$
- 142.** Given that:  
 $\text{Ni}^{2+}/\text{Ni} = 0.25 \text{ V}$ ,  $\text{Cu}^{2+}/\text{Cu} = 0.34 \text{ V}$ ,  
 $\text{Ag}^+/\text{Ag} = 0.80 \text{ V}$  and  $\text{Zn}^{2+}/\text{Zn} = -0.76 \text{ V}$
- Which of the following reactions under standard condition can take place in the specified direction?
- $\text{Cu}(\text{s}) + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag}(\text{aq})$
  - $\text{Ni}^{2+}(\text{aq}) + \text{Cu}(\text{s}) \rightarrow \text{Ni}(\text{s}) + \text{Cu}^{2+}(\text{aq})$
  - $\text{Zn}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 3\text{H}_2(\text{g})$
  - $\text{Cu}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
- 143.** Which of the following statement is/are not true for an electrochemical cell?
- $\text{H}_2$  is anode and Cu is cathode
  - $\text{H}_2$  is cathode and Cu is anode
  - reductions occurs at  $\text{H}_2$  electrode
  - oxidation occurs at Cu electrode
- 144.** Which of the following statements concerning the rusting of iron is true?
- The metal is reduced
  - The oxidation site can occur at a different place on the metal surface than the reduction site.
  - Salt increases the rate of corrosion by providing ions to carry the current.
  - The rusting of iron requires both oxygen and water.
- 145.** Regarding the requisites of an electrolyte to be used in a salt bridge, which of the following statements is/are correct?
- Low solubility of the electrolyte in water
  - High solubility of the electrolyte in water
  - Equal transport numbers of the cation and the anion of the electrolyte.
  - Large difference in the transport numbers.

- 146.** Which of the reaction/s is/are feasible?
- $2\text{KI} + \text{Br}_2 \rightarrow 2\text{KBr} + \text{I}_2$
  - $2\text{KBr} + \text{I}_2 \rightarrow 2\text{KI} + \text{Br}_2$
  - $2\text{KBr} + \text{Cl}_2 \rightarrow 2\text{KCl} + \text{Br}_2$
  - $2\text{H}_2\text{O} + 2\text{F}_2 \rightarrow 4\text{HF} + \text{O}_2$
- 147.** By passage of 1 F of electricity:
- 9 g of Al is deposited.
  - 5.6 L of  $\text{O}_2$  gas evolved at anode.
  - 0.5 mol of Cu is deposited.
  - 0.5 mol of Ca is deposited.
- 148.** Excess of KI reacts with  $\text{CuSO}_4$  solution and then  $\text{Na}_2\text{S}_2\text{O}_3$  solution is added to it. Which of the statements is/are correct for this reaction?
- $\text{Cu}_2\text{I}_2$  is formed
  - $\text{CuI}_2$  is formed
  - $\text{Na}_2\text{S}_2\text{O}_3$  is oxidized
  - evolved  $\text{I}_2$  is reduced
- 149.** Which of the following statements is/are not true for the electrochemical Daniel cell?
- Current flows from zinc electrode to copper electrode
  - Electrons flow from copper electrode to zinc electrode
  - Cations move toward zinc electrode
  - Cations move toward copper electrode
- 150.** Which of the following statement is/ are true?
- A fuel cell is a galvanic cell
  - One of the reactants in a fuel cell is a traditional fuel.
  - The cell reactants in a fuel cell are continuously supplied from an external source.
  - Modern fuel cells can be easily regenerated using household current.
- 151.** Consider Electrode potential data given below and select the statements which is/are not correct?
- $$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq}); E^\circ = +0.77 \text{ V}$$
- $$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s}); E^\circ = -1.66 \text{ V}$$
- $$\text{Br}_2(\text{aq}) + 2\text{e}^- \rightarrow \text{Br}^-(\text{aq}); E^\circ = +1.08 \text{ V}$$
- $\text{Fe}^{2+}$  is stronger reducing agent than  $\text{Br}^-$
  - $\text{Fe}^{2+}$  is stronger reducing agent than Al
  - Al is stronger reducing agent than  $\text{Fe}^{2+}$
  - $\text{Br}^-$  is stronger reducing agent than Al
- 152.** The standard reduction potentials of Zn and Ag in water are  $\text{Zn}^{2+} + 2\text{e}^- \leftrightarrow \text{Zn}; (E^\circ = -0.76 \text{ V})$  and  $\text{Ag}^+ + \text{e}^- \leftrightarrow \text{Ag}; (E^\circ = +0.80 \text{ V})$  at 298 K. Which of the following reaction is/are not feasible?
- $\text{Zn}^{2+}(\text{aq}) + \text{Ag}^+(\text{aq}) \rightarrow \text{Zn}(\text{s}) + \text{Ag}(\text{s})$
  - $\text{Zn}^{2+}(\text{aq}) + 2\text{Ag}(\text{s}) \rightarrow 2\text{Ag}^+(\text{aq}) + \text{Zn}(\text{s})$
  - $\text{Zn}(\text{s}) + \text{Ag}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Ag}^+(\text{aq})$
  - $\text{Zn}(\text{s}) + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$
- 153.** Which one of the following condition/s will not increase the voltage of the cell represented by the equation
- $$\text{Cu}(\text{s}) + 2\text{Ag}^+(\text{aq}) \leftrightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})?$$
- increase in the dimension of Cu electrode
  - increase in the dimension of Ag electrode
  - increase in the concentration of  $\text{Cu}^{2+}$  ions
  - increase in the concentration of  $\text{Ag}^+$  ions
- 154.** Lead storage battery contains
- Electrolyte as 38 %  $\text{H}_2\text{SO}_4$
  - Pb rod as cathode
  - Pb rod as anode
  - Pb plates coated with  $\text{PbO}_2$  act as cathode
- 155.** Which of these plots can not be obtained for a conductometric titration of a strong acid against a weak base?
- a.
- 
- b.
-



156. Which is/are true for standard electrode potentials?
- $E^\circ$  for oxidation is the negative of  $E^\circ$  for reduction.
  - Cell constituents are in their standard states.
  - The potential for the standard hydrogen electrode is chosen to be +1.00 V.
  - The half reactions are written as reductions.
157. For a galvanic cell at equilibrium, which of the following is/are not true?
- $E_{\text{cell}} = 0$
  - $\Delta H = 0$
  - $K_{\text{eq}} = 1$
  - $E_{\text{cell}} \neq 0$
158. The passage of electricity through certain electrolyte results in the liberation of  $H_2$  gas at the cathode. The electrolyte could be:
- $CuCl_2(aq)$
  - $NaCl(aq)$
  - $CaCl_2(aq)$
  - $AgNO_3(aq)$
159. For the galvanic cell  $Pt(s) | Sn^{2+}(aq), Sn^{4+}(aq) || Pb^{2+}(aq) | Pb(s)$ , what is/are not the function of the  $Pt(s)$ ?
- $Pt$  is the anode and does not appear in the overall cell reaction.
  - $Pt$  is the cathode and is a product in the overall cell reaction.
  - $Pt$  is the anode and is a reactant in the overall cell reaction.
  - $Pt$  is the cathode and does not appear in the overall cell reaction.
160. For the reduction of  $NO_3^-$  ion in an aqueous solution,  $E^\circ$  is +0.96 V. Values of  $E^\circ$  for some metal ions are given below.



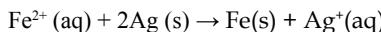
The pair of metals that is/are oxidized by  $NO_3^-$  in aqueous solution is/are

- V and Hg
- Hg and Fe
- Fe and Au
- Fe and V

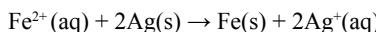
### Linked-Comprehension Type Questions

#### Comprehension 1

Given the following data:



Answer the following questions with respect to the reaction



161. What is  $E^\circ$  for the reaction?

- 12.4
- 1.24
- 6.2
- 62.0

162. If  $[Fe^{2+}] = 0.100 \text{ M}$  and  $[Ag^+] = 0.0100 \text{ M}$ , what is the magnitude  $E$  at 25°C?

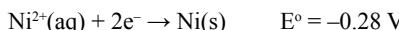
- 1.15V
- 11.5V
- 1.15 V
- 11.5V

163. For the reaction that is spontaneous, what is the maximum amount of work that can be performed?

- $3.3 \times 10^{-2} \text{ kwh}$
- $6.6 \times 10^{-2} \text{ kwh}$
- $12.2 \times 10^{-2} \text{ kwh}$
- $1.22 \times 10^{-2} \text{ kwh}$

#### Comprehension 2

Use the following data at 25°C for the questions given below



164. What is the standard cell potential for a voltaic cell constructed using the two half reaction.

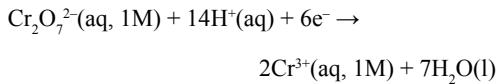
- 2.65 V
- 2.09 V
- 0
- 2.09 V

165. What is the cell potential if  $[Mg^{2+}] = 0.50\text{ M}$  and  $[Ni^{2+}] = 1.0\text{ M}$ ?
- 1.95 V
  - 2.00 V
  - 2.10 V
  - 2.08 V
166. What is K for the equilibrium at  $25^\circ\text{C}$ ?
- $4 \times 10^{-70}$
  - $4 \times 10^{70}$
  - $2 \times 10^{-35}$
  - $2 \times 10^{70}$

### Comprehension 3

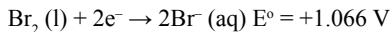
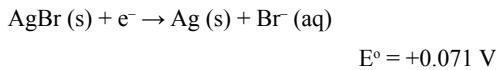
The emf, E, is related to the change in Gibbs free energy,  $\Delta G$ :  $\Delta G = -nFE$ , where n is the number of electrons transferred during the redox process and F is a unit called the Faraday. The faraday is the amount of charge on 1 mol of electrons:  $1\text{F} = 96,500\text{ C/mol}$ . Because E is related to  $\Delta G$ , the sign of E indicates whether a redox process is spontaneous:  $E > 0$  indicates a spontaneous process, and  $E < 0$  indicates a non-spontaneous one.

167. The standard electrode potential for the following reaction is  $+1.33\text{ V}$ . What is the potential at  $pH = 2.0$ ?



- $+2.184\text{ V}$
- $+0.5022\text{ V}$
- $+1.008\text{ V}$
- $+1.0542\text{ V}$

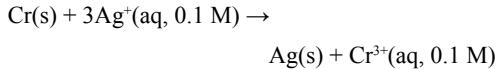
168.  $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$   $E^\circ = +0.800\text{ V}$



Use some of the above data to calculate  $K_{sp}$  at  $25^\circ\text{C}$  for  $\text{AgBr}$ .

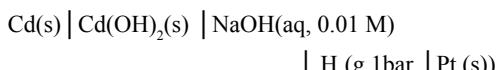
- $6.7 \times 10^{-12}$
- $2.8 \times 10^{-14}$
- $3.7 \times 10^{-19}$
- $4.9 \times 10^{-13}$

169. The  $E^\circ$  at  $298\text{ K}$  for the following reaction at the indicated concentrations is  $1.5\text{ V}$ . Find the  $\Delta G$  in  $\text{kJ}$  at  $298\text{ K}$ .



- $-422.83\text{ kJ}$
- $-212$
- $-295$
- $-140.94$

170. Given the cell:



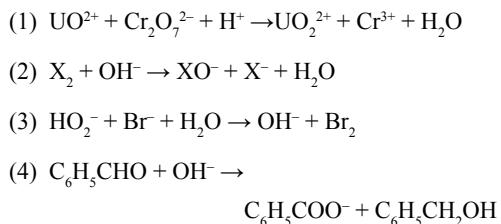
with  $E_{cell} = 0.0\text{V}$ . If  $E_{\text{Cd}}^{0, 2+} | \text{Cd} = -0.39\text{ V}$ , then  $K_{sp}$  of  $\text{Cd}(\text{OH})_2$  is:

- $10^{-15}$
- $10^{-13}$
- $10^{13}$
- $10^{15}$

### Comprehension 4

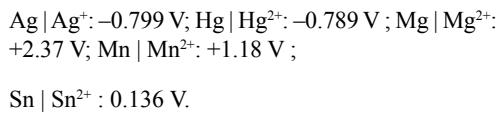
Redox reaction involve oxidation and reduction simultaneously. Redox are classified into four categories combination, decomposition, displacement, disproportionation reaction. The redox reaction have a great application in the study of various electrode processes, cells and in stoichiometric calculations etc.

171. Which of the following are disproportionation reactions?



- 1 and 2
- 2 and 3
- 3 and 4
- 2 and 4

172. Consider the following standard oxidation potentials (at  $25^\circ\text{C}$ ).

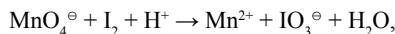


Which of the following statements is/are incorrect under standard conditions?

- Sn can displace Mg and Ag from their solutions.
- Ag can displace Hg and Mg from their solutions.
- Mn can displace Sn, Hg and Ag from their solutions.
- Mn can displace Sn, Mg and Hg from their solutions.

- (i), (ii), (iii)
- (ii), (iii), (iv)
- (i), (ii), (iv)
- (i), (ii), (iii), (iv)

173. In the redox reaction,



$\text{MnO}_4^\ominus$  and  $\text{I}_2$  would react in the molar ratio of:

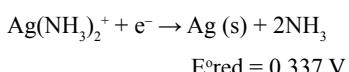
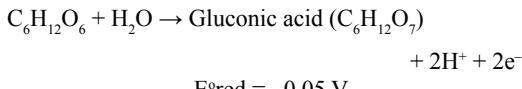
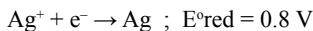
- 3 : 1
- 1 : 3
- 2 : 1
- 1 : 2

174. P, Q, R and S are four metals. P can displace R from its salt solution, but Q and R cannot displace S. Q can displace hydrogen (H) for a dilute solution of a mineral acid, but R cannot. The reduction potentials of P, Q, R, S and H (hydrogen) are in the order

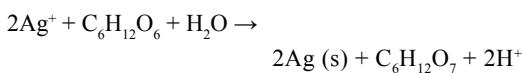
- a. H > P > R > S > Q
- b. P > S > Q > H > R
- c. P > Q > R > S > H
- d. R > H > Q > S > P

### Comprehension 5

Tollen's reagent is used for the detection of aldehydes when a solution of  $\text{AgNO}_3$  is added to glucose with  $\text{NH}_4\text{OH}$  then gluconic acid is formed.



[Use  $2.303 \times RT/F = 0.0592$  and  $F / RT = 38.92$  at 298 K]



175. Find K of this reaction.

- a. 66.13
- b. 58.38
- c. 28.30
- d. 46.29

[IIT 2006]

176. When ammonia is added to the solution, pH is raised to 11. Which half cell reaction is affected by pH and by how much?

- a.  $E^\circ_{\text{oxd}}$  will increase by a factor of 0.65 from  $E^\circ_{\text{oxd}}$ .
- b.  $E^\circ_{\text{oxd}}$  will decrease by a factor of 0.65 from  $E^\circ_{\text{oxd}}$ .
- c.  $E^\circ_{\text{red}}$  will increase by a factor of 0.65 from  $E^\circ_{\text{red}}$ .
- d.  $E^\circ_{\text{red}}$  will decrease by a factor of 0.65 from  $E^\circ_{\text{red}}$ .

[IIT 2006]

177. Ammonia is always added in this reaction. Which of the following must be incorrect?

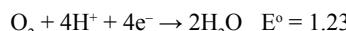
- a.  $\text{NH}_3$  combines with  $\text{Ag}^+$  to form a complex
- b.  $\text{Ag}(\text{NH}_3)_2^+$  is a stronger oxidizing reagent than  $\text{Ag}^+$ .

- c. In absence of  $\text{NH}_3$  silver salt of gluconic acid is formed
- d.  $\text{NH}_3$  has affected the standard reduction potential of glucose/gluconic acid electrode.

[IIT 2006]

### Comprehension 6

Redox reactions play a pivotal role in chemistry and biology. The values of standard redox potential ( $E^\circ$ ) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example of Daniel cell in which zinc goes into solution and copper gets deposited. Given below are a set of half cell reactions (acidic medium) along with their  $E^\circ$  (V with respect to normal hydrogen electrode) values. Using this data obtained the correct explanations.



178. Among the following, identify the correct statement.

- a. Chloride ion is oxidized by  $\text{O}_2$
- b.  $\text{Fe}^{2+}$  is oxidized by iodine
- c. Iodide ion is oxidized by chlorine
- d.  $\text{Mn}^{2+}$  is oxidized by chlorine

[IIT 2007]

179. While  $\text{Fe}^{3+}$  is stable,  $\text{Mn}^{3+}$  is not stable in acid solution because

- a.  $\text{O}_2$  oxidizes  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$
- b.  $\text{O}_2$  oxidizes both  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  and  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$
- c.  $\text{Fe}^{3+}$  oxidizes  $\text{H}_2\text{O}$  to  $\text{O}_2$
- d.  $\text{Mn}^{3+}$  oxidizes  $\text{H}_2\text{O}$  to  $\text{O}_2$

[IIT 2007]

180. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and  $\text{H}_2\text{SO}_4$  in presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of

- a.  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
- b.  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$
- c.  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_2$
- d.  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_3$

[IIT 2007]

### Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given. Mark

- a. if A and R both are correct and R is the correct explanation of A;
  - b. if A and R both are correct but R is not the correct explanation of A;
  - c. A is true but R is false;
  - d. A is false but R is true;
  - e. A and R both are false.
181. (A): In brown ring complex,  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}] \text{SO}_4$ , the oxidation number of iron is +1.  
(R): Due to charge transfer the one unpaired electron of NO shifts to  $\text{Fe}^{2+}$ , thereby  $\text{Fe}^{2+}$  converts into  $\text{Fe}^+$ .
182. (A): If standard reduction potential for the reaction  
 $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$  is 0.80 volts  
then for the reaction  
 $3\text{Ag}^+ + 3\text{e}^- \rightarrow 3\text{Ag}$   
it will be 2.4 volts  
(R): If concentration is increased, reduction electrode potential is increased.
183. (A): 1 faraday of electricity is passed through acidified  $\text{H}_2\text{O}$ , volume of  $\text{O}_2$  liberated at STP will be 5.6 L.  
(R): Equivalent weight of oxygen is 16.
184. (A): The voltage of mercury cell remains constant for longer period of time.  
(R): It is because net cell reaction does not involve any ion.
185. (A): The correct order of equivalent conductance at infinite dilution is  $\text{KCl} > \text{NaCl} > \text{LiCl}$   
(R): KCl is stronger electrolyte than NaCl which is stronger than LiCl.
186. (A): The tendency of an atom to reach a stable electronic arrangement may be satisfied by the transfer of electrons from one atom to another.  
(R): Loss and gain of electrons constitute reduction and oxidation.
187. (A): In acidic medium equivalent weight of  $\text{K}_2\text{Cr}_2\text{O}_7$  equals to 294 same as that of molecular weight.  
(R): In acidic medium  $\text{K}_2\text{Cr}_2\text{O}_7$  does not observe any change.

188. (A): For a weak electrolyte, the plot of molar conductivity ( $\Lambda_m$ ) against  $\sqrt{c}$  (c is concentration in mol lit<sup>-1</sup>) is nearly linear.  
(R): The molar conductivity at infinite dilution ( $\Lambda_m$ ) for an electrolyte can be considered equal to the sum of the limiting molar conductivities of the individual ions.
189. (A): Cell constant is the E.M.F. of a cell.  
(R): Cell constant is determined by using saturated KCl solution
190. (A): When acidified zinc sulphates solution is electrolyzed between zinc electrodes, it is zinc that is deposited at the cathode and hydrogen evolution does not take place.  
(R): The electrode potential of zinc is more negative than hydrogen as the over-voltage for hydrogen evolution on zinc is quite large.
191. (A): For three half-cell reactions involving different number of electrons.  $E_3 = E_1 + E_2$   
(R):  $\Delta G_3 = \Delta G_1 + \Delta G_2$
192. (A): The mobility of sodium ion is lower than that of potassium ion.  
(R): The ionic mobilities depend upon the effective radius of the ion.
193. (A): At the end of electrolysis using platinum electrodes, an aqueous solution of  $\text{CuSO}_4$  turns colourless.  
(R):  $\text{CuSO}_4$  changes stoichiometric  $\text{Cu}(\text{OH})_2$  during electrolysis.
194. (A): 1 faraday of electricity deposits 1 g equivalent of Ag or Cu or Al.  
(R): 1 mol electrons are required to reduce 1 mol of  $\text{Ag}^+$  or  $\text{Cu}^{2+}$  or  $\text{Al}^{3+}$  ion.
195. (A): When an aqueous solution of  $\text{NaNO}_3$  is electrolysed, sodium is liberated at the cathode.  
(R):  $\text{Na}^+$  ions are discharged at cathode and  $\text{NO}_3^-$  at the anode.
196. (A): When acidified zinc sulphate solution is electrolyzed between zinc electrodes. It is zinc that is deposited at the cathode and hydrogen evolution does not take place.  
(R): The electrode potential of zinc is more negative than hydrogen as the overvoltage for hydrogen evolution on zinc is quite large.
197. (A): At the end of electrolysis using platinum electrodes, an aqueous solution of copper sulphate turn colourless.  
(R): Copper in copper sulphate is converted to copper hydroxide during the electrolysis.

## 6.48 ■ Electrochemistry

**198. (A):** Poggendorff compensation method is used for the measurement of emf of voltaic cells

**(R):** This method has the advantage of giving the emf an open circuit when it produces no current and thus of determining emf of cells under reversible condition.

**199. (A):** Equivalent conductance increases with dilution for an electrolyte solution while its specific conductance decreases.

**(R):** The number of ions in one litre of electrolyte increases with dilution.

**200. (A):** Any cell having  $E^\circ_{\text{cell}} = 5.91$ .

Volt, will have equilibrium constant  $10^3$  at 298 K.

**(R):** As at 298 K,  $K_{\text{eq}}$

$$= 10 (E^\circ_{\text{cell}} / 0.0591).$$

### Matrix-Match Type Questions

**201.** Match the following:

Column I	Column II
A. $\Lambda_m(p)$	$1/k \times l/a$
B. k	$(p) 1/k \times l/a$
C. $\alpha$	$(q) \Lambda^\vee / \Lambda^\circ$
D. $\Lambda_E$	$(r) \frac{k \times 1000}{N}$
	$(s) \frac{k \times 1000}{m}$
	$(t) \text{increase with dilution}$

**202.** Match the following:

Column I	Column II
A. $\text{H}_2\text{SO}_5$	$(p) +6 \text{ oxidation state}$
B. $\text{CrO}_5$	$(q) \text{ peroxy linkage}$
C. $\text{K}_2\text{Cr}_2\text{O}_7$	$(r) \text{Oxidant}$
D. $\text{H}_2\text{O}_2$	$(s) \text{ Bleaching action}$

**203.** Match the following:

Column I	Column II
A. Electrode reversible with respect to cation	$(p) \text{Pt}/\text{Fe}^{2+}, \text{Fe}^{3+}$
B. Electrode reversible with respect to anion	$(q) \text{Pt}, \text{H}_2 (1 \text{ atm})/\text{H}^+$ $(a = 1)$

C. Redox electrode  $(r) \text{Ag}/\text{AgCl} (\text{s}), \text{HCl} (\text{aq})$

D. Reference electrode  $(s) \text{Ag}/\text{AgNO}_3$   
 $(t) E^\circ \text{ is zero}$

**204.** Match the following:

Column I	Column II
A. $\text{Zn}   \text{Zn}^{2+}    \text{Cu}^{2+}   \text{Cu}$	$(p) \text{chemical cell with transference}$
B. $\text{H}_2 (\text{g}, \text{P}_{\text{H}_2})   \text{HCl} \text{ a.}, \text{AgCl} (\text{s}), \text{Ag}$	$(q) \text{chemical cell without transference}$
C. $\text{H}_2 (\text{g}, \text{P}_{\text{H}_2})   \text{H}^+(\text{a}_1)   \text{H}^+(\text{a}_2)   \text{H}_2 (\text{g}, \text{P}_{\text{H}_2})$	$(r) \text{concentration cell with transference}$
D. $\text{H}_2 (\text{g}, \text{P}_1)   \text{H}^+\text{a.}   \text{H}_2 (\text{g}, \text{P}_2)$	$(s) \text{concentration cell without transference}$

**205.** Match the following:

Column I	Column II
A. A gas in contact with an inert electrode	$(p) \text{electrode potential}$
B. the potential difference in volts between the two electrodes	$(q) \text{O}_2 \text{ at anode metal and the solution of metal ion}$
C. Li metal has the lowest standard electrode	$(r) \text{H}_2(\text{g})/\text{Pt} \text{ potential}$
D. electrolysis of aq. $\text{Na}_2\text{SO}_4$ using Pt electrodes	$(s) \text{strongest reducing agent}$
	$(t) -3.06 \text{ Volt}$

**206.** Match the following:

Column I	Column II
A. Dry cell	$(p) \text{Primary cell}$
B. Mercury cell	$(q) \text{Secondary cell}$
C. Lead storage Battery	$(r) \text{Electro chemical cell}$
D. Ni-Cd cell	$(s) 12 \text{ volt}$
	$(t) 1.35 \text{ volt}$

**207.** Match the following:

Column I	Column II
A. electrolysis of aq. $\text{NaOH}$	$(p) \text{reduction of H}^+ \text{ and oxidation of OH}^-$
B. electrolysis of $\text{CuCl}_2$ with $\text{Cu}$ electrode	$(q) \text{Cu at cathode and O}_2 \text{ at anode}$

C. electrolysis of  $\text{H}_2\text{O}$  (r)  $\text{H}_2$  at cathode and  $\text{O}_2$  at anode

D. electrolysis of aq.  $\text{CuSO}_4$  (s) weight of cathode decreases  
(t) increases and weight of anode

**208.** Match the following:

<b>Column I</b>	<b>Column II</b>
A. anode	(p) $E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$
B. conductance	(q) mass of product deposited by 1 coulomb of electricity
C. electrochemical equivalent	(r) $(\text{resistance})^{-1}$
D. $E^\circ_{\text{cell}}$	(s) involves oxidation (t) molecular weight of ion

**209.** Match the following:

<b>Column I</b>	<b>Column II</b>
A. electrolytic cell	(p) Nernst equation
B. $E_{\text{cell}} =$	(q) 96500 coulombs
$\frac{0.059}{n} \log \frac{\text{Cathode}}{\text{Canode}}$	
C. connect two half cells	(r) EMF of cell
D. 1 faraday	(s) salt bridge (t) device converting electrical energy into chemical energy

**210.** Match the following:

<b>Column I (Reactions)</b>	<b>Column II (Nature of reactions/type)</b>
A. $\text{O}_2^- \rightarrow \text{O}_2 + \text{O}_2^{2-}$	(p) redox reaction
B. $\text{CrO}_4^{2-} + \text{H}^+ \rightarrow$	(q) one of the products has trigonal planar structure
C. $\text{MnO}_4^- + \text{NO}_2^- + \text{H}^+ \rightarrow$	(r) dimeric bridged tetrahedral metal ion
D. $\text{NO}_3^- + \text{H}_2\text{SO}_4 + \text{Fe}^{2+} \rightarrow$	(s) disproportionation

### The IIT-JEE Corner

**211.** A standard hydrogen electrode has zero electrode potential because

- a. hydrogen is easiest to oxidize
- b. this electrode potential is assumed to be zero
- c. hydrogen atom has only one electron
- d. hydrogen is the lightest element

[IIT 1997]

**212.** The standard reduction potentials of  $\text{Cu}^{2+}/\text{Cu}$  and  $\text{Cu}^{2+}/\text{Cu}^+$  are 0.337 V and 0.153 V respectively. The standard electrode potential of  $\text{Cu}^+/\text{Cu}$  half cell is

- a. 0.184 V
- b. 0.827 V
- c. 0.521 V
- d. 0.490 V

[IIT 1997]

**213.** The standard reduction potential values of three metallic cations X, Y, and Z are 0.52, -3.03 and -1.18 respectively. The order of reducing power of the corresponding metal is

- a.  $\text{Y} > \text{Z} > \text{X}$
- b.  $\text{X} > \text{Y} > \text{Z}$
- c.  $\text{Z} > \text{Y} > \text{X}$
- d.  $\text{Z} > \text{X} > \text{Y}$

[IIT 1998]

**214.** A gas at 1 atm is bubbled through a solution containing a mixture of 1 M  $\text{Y}^-$  and 1 M  $\text{Z}^-$  at 25°C. If the reduction potential of  $\text{Z} > \text{Y} > \text{X}$ , then

- a. Y will oxidise X and not Z
- b. Y will oxidise Z and not X
- c. Y will oxidise both X and Z
- d. Y will reduce both X and Z

[IIT 1999]

**215.** The oxidation number of sulphur in  $\text{S}_8$ ,  $\text{S}_2\text{F}_2$ ,  $\text{H}_2\text{S}$  respectively, are

- a. 0, +1 and -2
- b. +2, +1 and -2
- c. 0, +1 and +2
- d. -2, +1 and -2.

[IIT 1999]

**216.** For the electrochemical cell,  $\text{M} | \text{M}^+ \parallel \text{X}^- | \text{X}, E^\circ_{\text{M}^+/\text{M}} = 0.44 \text{ V}$  and  $E^\circ_{\text{X}^-/\text{X}} = 0.33 \text{ V}$ .

From these data one can deduce that

- a.  $\text{M} + \text{X} \rightarrow \text{M}^+ + \text{X}^-$  is the spontaneous reaction
- b.  $\text{M}^+ + \text{X}^- \rightarrow \text{M} + \text{X}$  is spontaneous reaction
- c.  $E_{\text{cell}} = 0.77 \text{ V}$
- d.  $E_{\text{cell}} = -0.77 \text{ V}$

[IIT 2000]

## 6.50 ■ Electrochemistry

217. Among the following, identify the species with an atom in +6 oxidation state:

- a.  $\text{MnO}_4^-$
- b.  $\text{Cr}(\text{CN})_6^{3-}$
- c.  $\text{NiF}_6^{2-}$
- d.  $\text{CrO}_2\text{Cl}_2$

[IIT 2000]

218. Saturated solution of  $\text{KNO}_3$  is used to make ‘salt bridge’ because:

- a. velocity of  $\text{K}^+$  is greater than that of  $\text{NO}_3^-$ .
- b. velocity of  $\text{NO}_3^-$  is greater than that of  $\text{K}^+$ .
- c. velocities of both  $\text{K}^+$  and  $\text{NO}_3^-$  are nearly the same.
- d.  $\text{KNO}_3$  is highly soluble in water.

[IIT 2001]

219. The reaction,



is an example of

- a. oxidation reaction
- b. reduction reaction
- c. disproportionation reaction
- d. decomposition reaction

[IIT 2001]

220. The correct order of equivalent conductance at infinite dilution of  $\text{LiCl}$ ,  $\text{NaCl}$  and  $\text{KCl}$  is:

- a.  $\text{LiCl} > \text{NaCl} > \text{KCl}$
- b.  $\text{KCl} > \text{NaCl} > \text{LiCl}$
- c.  $\text{NaCl} > \text{KCl} > \text{LiCl}$
- d.  $\text{LiCl} > \text{KCl} > \text{NaCl}$

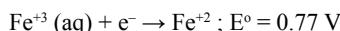
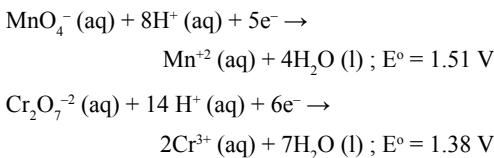
[IIT 2001]

221. In the standardization of  $\text{Na}_2\text{S}_2\text{O}_3$  using  $\text{K}_2\text{Cr}_2\text{O}_7$  by iodometry, the equivalent weight of  $\text{K}_2\text{Cr}_2\text{O}_7$  is:

- a. (molecular weight) / 2
- b. (molecular weight) / 6
- c. (molecular weight) / 3
- d. same as molecular weight

[IIT 2001]

222. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below:



Identify the only incorrect statement regarding the quantitative estimation of aqueous  $\text{Fe}(\text{NO}_3)_2$ .

- a.  $\text{MnO}_4^-$  can be used in aqueous  $\text{HCl}$
- b.  $\text{Cr}_2\text{O}_7^{2-}$  can be used in aqueous  $\text{HCl}$
- c.  $\text{MnO}_4^-$  can be used in aqueous  $\text{H}_2\text{SO}_4$
- d.  $\text{Cr}_2\text{O}_7^{2-}$  can be used in aqueous  $\text{H}_2\text{SO}_4$

[IIT 2002]

223. In the electrolytic cell, flow of electrons is from:

- a. cathode to anode in solution.
- b. cathode to anode through external supply.
- c. cathode to anode through internal supply.
- d. anode to cathode through internal supply.

[IIT 2003]

224. The pair of the compounds in which both the metals are in the highest possible oxidation state is

- a.  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Co}(\text{CN})_6]^{3-}$
- b.  $[\text{Co}(\text{CN})_6]^{3-}$ ,  $\text{MnO}_2$
- c.  $\text{TiO}_3$ ,  $\text{MnO}_2$
- d.  $\text{CrO}_2\text{Cl}_2$ ,  $\text{MnO}_4^-$

[IIT 2004]

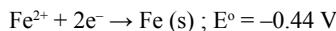
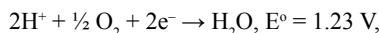
225. The emf of the cell

$\text{Zn} | \text{Zn}^{2+} (0.01 \text{ M}) || \text{Fe}^{2+} (0.001 \text{ M}) | \text{Fe}$  at 298 K is 0.2905 volt. Then the value of equilibrium constant for the cell reaction is

- a.  $e^{0.32/0.0295}$
- b.  $10^{0.32/0.0295}$
- c.  $10^{0.26/0.0295}$
- d.  $10^{0.32/0.0591}$

[IIT 2004]

226. The half-cell reaction for the corrosion



Find the  $\Delta G^\circ$  (in kJ) for the overall reaction.

- a. -76
- b. -322
- c. -161
- d. -152

[IIT 2005]

227. We have taken a saturated solution of  $\text{AgBr}$ .  $K_{\text{sp}}$  of  $\text{AgBr}$  is  $12 \times 10^{-14}$ . If  $10^{-7}$  mole of  $\text{AgNO}_3$  are added to 1 litre of this solution find conductivity (specific conductance) of this solution in terms of  $10^{-7} \text{ S m}^{-1}$  units.

Given  $\lambda^\circ(\text{Ag}^+) = 6 \times 10^{-3} \text{ Sm}^2 \text{ mol}^{-1}$ ,  
 $\lambda^\circ(\text{Br}^-) = 8 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$ ,  
 $\lambda^\circ(\text{NO}_3^-) = 7 \times 10 \text{ S m}^2 \text{ mol}^{-1}$ .

- a. 55                    b. 5.5  
c. 110                   d. 27

[IIT 2006]

228. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenyl amine as indicator. The number of moles of Mohr's salt required per mole of dichromate is:

- a. 3                    b. 4  
c. 5                    d. 6

[IIT 2007]

229. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 mA current. The time required to liberate 0.01 mole of H<sub>2</sub> gas at the cathode is (1 Faraday = 96500 C mol<sup>-1</sup>)

- a.  $9.65 \times 10^4$  s                    b.  $19.3 \times 10^4$  s  
c.  $28.95 \times 10^4$  s                    d.  $38.6 \times 10^4$  s

[IIT 2008]

## ANSWERS

### Straight Objective Type Questions

- |       |       |       |       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1. c  | 2. d  | 3. b  | 4. b  | 5. d  | 6. c  | 7. d  | 8. c  | 9. a  | 10. b |
| 11. d | 12. d | 13. c | 14. a | 15. c | 16. b | 17. b | 18. c | 19. d | 20. a |
| 21. b | 22. b | 23. a | 24. c | 25. b | 26. c | 27. c | 28. a | 29. d | 30. a |
| 31. b | 32. d | 33. d | 34. c | 35. b | 36. b | 37. c | 38. b | 39. c | 40. c |
| 41. a | 42. c | 43. d | 44. d | 45. c | 46. a | 47. b | 48. c | 49. c | 50. a |
| 51. d | 52. a | 53. a | 54. c | 55. b | 56. b | 57. b | 58. a | 59. a | 60. d |
| 61. a | 62. a | 63. d | 64. c | 65. d | 66. c | 67. c | 68. b | 69. b | 70. b |
| 71. c | 72. d | 73. d | 74. b | 75. d | 76. b | 77. b | 78. b | 79. a | 80. b |

### Brainteasers Objective Type Questions

- |        |        |        |        |        |        |        |        |        |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 81. a  | 82. c  | 83. b  | 84. a  | 85. c  | 86. a  | 87. c  | 88. c  | 89. a  |
| 90. c  | 91. b  | 92. a  | 93. a  | 94. b  | 95. c  | 96. c  | 97. d  | 98. c  |
| 99. d  | 100. b | 101. b | 102. d | 103. a | 104. b | 105. a | 106. b | 107. d |
| 108. b | 109. a | 110. a | 111. c | 112. a | 113. b | 114. d | 115. b | 116. c |
| 117. d | 118. a | 119. a | 120. c | 121. b | 122. b | 123. d | 124. b | 125. d |
| 126. a | 127. c | 128. c | 129. b | 130. a | 131. a | 132. c | 133. c | 134. a |
| 135. a |        |        |        |        |        |        |        |        |

### Multiple Correct Answer Type Questions

- |              |              |              |              |              |                 |
|--------------|--------------|--------------|--------------|--------------|-----------------|
| 136. a, b, c | 137. a, b    | 138. a, c, d | 139. a, b, c | 140. b, c, d | 141. b, c, d    |
| 142. a, c    | 143. b, c, d | 144. b, c, d | 145. b, c    | 146. a, c, d | 147. a, b, c, d |
| 148. a, c, d | 149. a, b, c | 150. a, b, c | 151. b, d    | 152. a, b, c | 153. a, b, c    |
| 154. a, c, d | 155. a, b, d | 156. a, b, d | 157. b, c, d | 158. b, c    | 159. b, c, d    |
| 160. a, b, d |              |              |              |              |                 |

**Linked-Comprehension Type Questions****Comprehension 1**

161. b      162. c      163. b

**Comprehension 2**

164. d      165. c      166. b

**Comprehension 3**

167. d      168. d      169. a      170. a

**Comprehension 4**

171. d      172. c      173. c      174. d

**Comprehension 5**

175. b      176. a      177. d

**Comprehension 6**

178. c      179. d      180. a

**Assertion Reason Type Answers**

181. a      182. d      183. c      184. a

185. b      186. c      187. e      188. d

189. d      190. a      191. d      192. c

193. c      194. c      195. d      196. a

197. c      198. a      199. c      200. a

**Matrix-Match Type Questions**

201. A - (s, t), B - (p), C - (q), D - (r, t)

203. A - (s), B - (r), C - (p), D - (q)

205. A - (r), B - (p), C - (s), D - (q)

207. A - (r), B - (s), C - (p), D - (q)

209. A - (t), B - (r), C - (s), D - (q)

202. A - (p, q, r), B - (p, q, r), C - (p, r), D - (p, q, r, s)

204. A - (p), B - (q), C - (r), D - (s)

206. A - (p, r), B - (q, r, t), C - (q, r, s), D - (q, r)

208. A - (s), B - (r), C - (q), D - (p)

210. A - (p, s), B - (r), C - (p, q), D - (p)

**The IIT-JEE Corner**

211. b      212. c      213. a

219. c      220. b      221. b

227. a      228. d      229. d

214. a

222. a

215. a

223. c

216. b

224. d

217. d

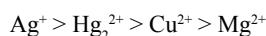
225. b

218. c

226. b

**Hints and Explanations**

- More negative is the reduction potential, higher is the reducing property, that is, the power to give up electrons
- The reduction potentials (as given) of the ions are in the order:



$\text{Mg}^{2+}$  (aq) will not be reduced as its reduction potential is much lower than water ( $-0.83\text{ V}$ )

Hence the sequence of deposition of the metals will be Ag, Hg, Cu.

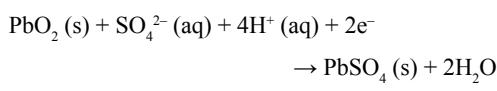
- Anodic reaction:  

$$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$$
- Cathodic reaction:  

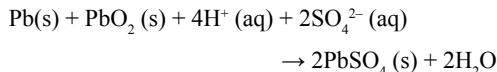
$$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$$
- Here pH of 0.1 M HCl and 0.1 M  $\text{CH}_3\text{COOH}$  is not same i.e., different concentration so emf of this cell will not be zero.
- Reactions during discharging of lead storage battery are:  
An anode  

$$\text{Pb(s)} + \text{SO}_4^{2-} \text{(aq)} \rightarrow \text{PbSO}_4 \text{(s)} + 2\text{e}^-$$

At cathode

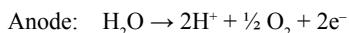
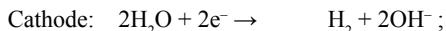


Net reaction



Thus  $\text{H}_2\text{SO}_4$  is consumed in this reaction.

7. Water is reduced at the cathode and oxidized at the anode instead of  $\text{Na}^+$  and  $\text{SO}_4^{2-}$ .



8. The given values are oxidation potential. On Changing these to reduction potential values

$$\text{EMF} = E^\circ_c - E^\circ_a$$

$$= E^\circ_{\text{Fe}^{2+}/\text{Fe}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}}$$

$$= -0.41 - (-0.76)$$

$$= -0.41 + 0.76 = 0.35 \text{ V}$$

10. Copper is more reactive than Ag, so it displaces silver from  $\text{AgNO}_3$ ,



$$11. E^\circ_{\text{cell}} = E^\circ_c - E^\circ_a$$

$$= -0.44 - (-0.14)$$

$$= -0.44 + 0.14$$

$$= -0.30 \text{ V}$$

13. Mg and Al have lower reduction potential than water. So water is reduced more easily to give  $\text{H}_2$  gas at the cathode.

14.  $\frac{\text{Mass of hydrogen}}{\text{Mass of copper}}$

$$= \frac{\text{Eq. mass of hydrogen}}{\text{Eq. mass of copper}}$$

$$\frac{0.504 \text{ g}}{m_{\text{Cu}}} = \frac{1}{(63.5 / 2)}$$

$$m_{\text{Cu}} = \frac{0.504 \text{ g} \times 63.5}{2} = 16.0 \text{ g}$$

16. Number of faraday =  $\frac{It}{96500}$

$$= \frac{80 \times 10^{-6} \times 100 \times 24 \times 60 \times 60}{96500}$$

$$= 7.16 \times 10^{-3}$$

17.  $\Lambda_{\text{eq}} = \frac{k}{c_{\text{eq}}} = \frac{0.0041 \text{ mho cm}^{-1}}{0.01 \text{ eq L}^{-1}}$   
 $= \frac{0.00419 \times 1000}{0.01} \text{ mho cm}^2 \text{ eq}^{-1}$   
 $(1 \text{ L} = 1000 \text{ cm}^2)$   
 $= 419 \text{ mho cm}^2 \text{ eq}^{-1}$ .

18.  $\text{O}_2\text{PtF}_6$  can be written as  $\text{O}_2^+[\text{PtF}_6]^-$ . In this compound oxidation state of Pt is +6 and  $\text{O}_2$  carries a charge of +1.

Let X = oxidation state of oxygen in

$$\text{O}_2^+ \text{So } 2X = +1$$

$$X = +\frac{1}{2}$$

20. During the electrolysis of aq.  $\text{Na}_2\text{SO}_4$ ,  $\text{H}_2$  is evolved at the cathode as  $E^\circ_{\text{R.P.}}$  of sodium (-2.71 V) is much lower than that of water (-0.83 V) while  $\text{O}_2$  is evolved at the anode as  $E^\circ_{\text{R.P.}}$  potential of  $\text{SO}_4^{2-}$  ion (-0.2 V) is much less than that of water (-1.23 V).

23. The equivalent conductance of  $\text{BaCl}_2$  at infinite dilution.

$$\lambda_\infty \text{ of BaCl}_2 = \frac{1}{2} \lambda_\infty \text{ of Ba}^{2+} + \lambda_\infty \text{ of Cl}^-$$

$$= \frac{127 + 76}{2} = 139.5 \text{ ohm}^{-1} \text{ cm}^2$$

25. emf of the cell ( $E_{\text{cell}}$ ) = Ecathode – Eanode

$$= -0.76 - 0.41 = -1.17 \text{ V}$$

26.  $\Delta G^\circ = -nF E^\circ_{\text{cell}} = -2 \times 96500 \times 1.1$

$$= -212300 \text{ J} = -212.3 \text{ kJ}$$

27.  $\text{Fe}^{2+} / \text{Fe} \quad E^\circ = -0.44$

- $\text{Fe}^{3+} / \text{Fe}^{2+} \quad E^\circ = 0.77$

The metals having higher negative electrode potential can displace metals having lower values of negative electron potential from their salt solutions.

29. 11.2 lit. of hydrogen is liberated by 96500 C (1 faraday) of charge.

So 0.112 litre of hydrogen is liberated by a charge of

$$\frac{96500}{112} \times 0.112 = 965 \text{ C.}$$

30. When the concentration of  $\text{Ag}^+$  ions increases, then voltage of the cell also increases due to an increase in the collisions of ions.

## 6.54 ■ Electrochemistry

31. In electrolysis of NaCl when Pt electrode is taken then H<sub>2</sub> liberated at cathode while with Hg cathode it forms sodium amalgam because more voltage is required to reduce H<sup>+</sup> at Hg than Pt.

33. Oxidation no. of Fe in [Fe(H<sub>2</sub>O)<sub>5</sub>(NO)]<sup>2+</sup>

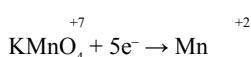
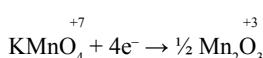
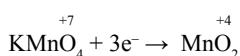
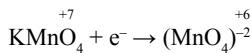
$$= x + 0 + 1 = 2$$

$$x = 2 - 1 = +1$$

35. ZnO + C → Zn + CO, ΔG° = -ve

So this is spontaneous.

36.



37. ΔG = -nEF

For 1 mol of Al, n = 3

For 4/3 mol of Al, n = 3 × 4/3 = 4

According to the question,

$$827 \times 1000 = 4 \times E \times 96500$$

$$\text{or } E = 2.14 \text{ V}$$

38. According to Faraday's second law of electrolysis,

$$\frac{W_{\text{Ag}}}{W_{\text{H}}} = \frac{E_{\text{Ag}}}{E_{\text{H}}}$$

$$WH = \frac{1.08 \times 1}{108} = 0.01 \text{ g}$$

Since 2 g of hydrogen at STP has a volume of 22.4 litres, therefore volume of 0.01 g of hydrogen at STP

$$= \frac{22.4}{2} \times 0.01 = 0.112 \text{ litre} = 112 \text{ ml}$$

39. Cell concentration is Zn + Cu<sup>2+</sup> → Zn<sup>2+</sup> + Cu

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

greater the factor [(Zn<sup>2+</sup>) / (Cu<sup>2+</sup>)], less is the EMF.  
So E<sub>1</sub> > E<sub>2</sub>.

40. The given cell is represented as:

Pt | H<sub>2</sub> (g) | HCl (soln) || AgCl (s) | Ag, as H<sub>2</sub> undergoes oxidation and AgCl (Ag<sup>+</sup>) undergoes reduction in this representation.

$$41. E_{\text{cell}} = \frac{E_{\text{cell}}^{\circ}}{N} - 0.0591 \log \frac{\text{Zn}^{2+}}{\text{Cu}^{2+}}$$

$$= 1.1 - \frac{0.0591}{2} \log \frac{0.1}{0.1}$$

$$= 1.1 - 0.02955 \log 1$$

$$= 1.1 - 0.02955 \times 0 = 1.1 \text{ V}$$

$$42. E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log Q$$

$$\text{Cu} + \text{Zn} \rightarrow \text{Zn} + \text{Cu}$$

$$0.1 \text{ M} \quad 1 \text{ M}$$

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{1}{0.1} = 10$$

$$E_{\text{cell}} = 1.10 - \frac{0.0591}{2} \log 10$$

$$= 1.10 - 0.0295$$

$$= 1.0705 \text{ V}$$

$$43. E_{\text{cell}}^{\circ} = \frac{2.303 RT}{nF} \log K_{\text{eq}}$$

$$0.295 = \frac{0.0591}{2} \log K_{\text{eq}}$$

$$\log K_{\text{eq}} = 10$$

$$K_{\text{eq}} = 10^{10}$$

$$44. \frac{\text{Wt. of Ag deposited}}{\text{Wt. of O}_2 \text{ produced}} = \frac{108}{8}$$

$$\frac{0.108}{\text{Wt. of O}_2} = \frac{108}{8}$$

So weight of O<sub>2</sub> produced = 8 × 10<sup>-3</sup> g

$$= \frac{22400}{32} \times 8 \times 10^{-3} \text{ cm}^3 = 5.6 \text{ cm}^3$$

$$45. E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \frac{\ln [\text{Zn}^{2+}][\text{Cl}^-]^2}{\text{PCl}_2}$$

46. In the given reaction, I<sup>-</sup> has been oxidized to I<sub>2</sub> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ions have been reduced to Cr<sup>3+</sup>.

$$E_{\text{cell}}^{\circ} = E_{\text{Cr}_2\text{O}_7^{2-}}^{\circ} - E_{\text{I}_2}^{\circ}$$

$$0.79 = 1.33 - E_{\text{I}_2}^{\circ}$$

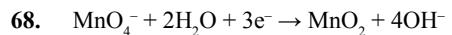
$$E_{\text{I}_2}^{\circ} = 0.54 \text{ V}$$

$$47. \text{Ionic mobility} = \frac{\text{Ionic conductance}}{96500}$$

$$= \frac{5 \times 10^{-4}}{96500} = 5.18 \times 10^{-9} \text{ cm/sec.}$$



## 6.56 ■ Electrochemistry



Charge required for the reduction of 1 mol of  $\text{MnO}_4^-$  to  $\text{MnO}_2$  = 3F (as charge = nF).

69. Electrochemical equivalent is the weight deposited by 1 coulomb.

$$Q = I \times t$$

$$1 = I \times 0.25$$

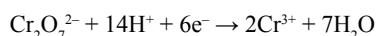
$$\text{So } I = 4 \text{ A.}$$

70.  $\Lambda^{\circ}_{\text{m}}(\text{CaCl}_2) = \lambda^{\circ}_{\text{m}}(\text{Ca}^{2+}) + 2\lambda^{\circ}_{\text{m}}(\text{Cl}^-)$   
 $= 118.88 \times 10^{-4} + 2(77.33 \times 10^{-4})$   
 $= 273.54 \times 10^{-4} \text{ m}^2 \text{ mho mol}^{-1}$

71. It is a concentration cell

$$E_{\text{cell}} = \frac{0.0591}{n} \log_{10} \frac{C_2 (\text{RHS})}{C_1 (\text{LHS})}$$
  
 $= \frac{0.0591}{1} \log_{10} \frac{0.1}{0.01} = 0.0591 \text{ V}$

72. Reduction of  $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{Cr}^{3+}$  is a  $6\text{e}^-$  change,



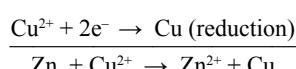
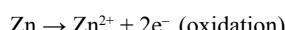
Thus, equivalent weigh of  $\text{Cr}_2\text{O}_7^{2-}$

= Mol. weight/6.

74. Electrode potential of cell must be +ve for spontaneous reaction.



Redox reaction is

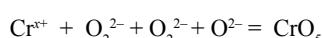


75.  $E^{\circ} = \frac{0.0591}{n} \log_{10} K$

here, n = 2,  $E^{\circ} = 0.295$

$$\log_{10} K = \frac{2 \times 0.295}{0.0591} \text{ or } K = 10^{10}$$

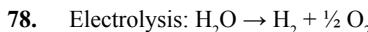
76. It comprises of the following things.



Peroxide Oxide

So, x is + 6

77. The potential is not affected if the reaction is multiplied by any integer. It is an intensive property.



1 mole of water on decomposition gives two equivalents of oxygen.

Quantity of electricity required

$$= 2 \times 96500 \text{ coulombs.}$$

$$\begin{aligned} \text{Time required} &= \frac{2 \times 96500}{2} = 96500 \text{ sec} \\ &= \frac{96500}{60 \times 60} = 26.8 \text{ hours} \end{aligned}$$

### Brainteasers Objective Type Questions

81.  $E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303 \text{ RT}}{nF} \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$

$$E_1 = E^{\circ}_{\text{cell}} - \frac{2.303 \text{ RT}}{2F} \log_{10} \frac{1}{1} = E^{\circ}_{\text{cell}}$$

$$E_2 = E^{\circ}_{\text{cell}} - \frac{2.303 \text{ RT}}{2F} \log_{10} \frac{0.1}{1.0}$$

$$E_3 = E^{\circ}_{\text{cell}} - \frac{2.303 \text{ RT}}{2F} \log_{10} \frac{1}{0.1}$$

Hence  $E_2 > E_1 > E_3$

82. As 22400 mL of hydrogen at STP (or NTP) = 2 g

So 112 mL of hydrogen at STP

$$= \frac{2 \text{ g} \times 112 \text{ mL}}{22400 \text{ mL}} = 10^{-2} \text{ g}$$

$$\begin{array}{ll} 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 & \\ 2\text{F} & 1 \text{ mol} \end{array}$$

$$= 2 \times 96500 \text{ C} = 2 \text{ g}$$

2 g hydrogen is deposited by =  $2 \times 96500 \text{ C}$   $10^{-2} \text{ g}$   
hydrogen will be deposited by

$$= \frac{2 \times 96500 \times 10^{-2} \text{ g}}{2 \text{ g}} = 965 \text{ C}$$

Charge (Q) = I.t

$$I = \frac{Q}{t} = \frac{965 \text{ C}}{965 \text{ s}} = 1 \text{ Cs}^{-1} = 1 \text{ A}$$

83.  $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$

$$3\text{F} \quad 1 \text{ mol} = 27.0 \text{ g}$$

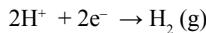
$$= 3 \times 96500 \text{ C}$$

The required charge

$$= \frac{40.5 \text{ g} \times 3 \text{ mol} \times 96500 \text{ C mol}^{-1}}{27.0 \text{ g}}$$

$$= 4.34 \times 10^5 \text{ C}$$

84.  $\text{pH} = 3.0$  or  $[\text{H}^+] = 10^{-3} \text{ M}$



$$\text{E}_{\text{H}^+/\text{H}_2} = \text{E}^\circ_{\text{H}^+/\text{H}_2} - \frac{0.059}{2}$$

$$\log_{10} \frac{1}{[\text{H}^+]^2}$$

$$= 0.0 \text{ V} - \frac{0.059}{2} \log_{10} \frac{1}{(10^{-3})^2}$$

$$= 0.0 \text{ V} - \frac{0.059}{2} \log_{10} (10^3)^2$$

$$= \frac{-0.059}{2} \times 6 = -0.177 \text{ V}$$

85. (i)  $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$

$$\begin{array}{ll} 1 \text{ mol} = 1 \text{ F} & 1 \text{ mol} \\ 3 \text{ F} & 3 \text{ mol} \end{array}$$

(ii)  $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$

$$\begin{array}{ll} 2 \text{ mol} = 2\text{F} & 1 \text{ mol} \\ 3 \text{ F} & 3/2 \text{ mol} \end{array}$$

(iii)  $\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Cr}(\text{s})$

$$3 \text{ mol} = 3\text{F} \quad 1 \text{ mol}$$

The required ratio of moles of Ag, Ni and Cr is: 3 mol Ag : 3/2 mol Ni: 1 mol Cr

that is, 6 mol Ag : 3 mol Ni : 2 mol Cr (6 : 3 : 2)

86. At STP mass of 22.4 L  $\text{H}_2 = 2 \text{ g}$

Mass of 2.24 L  $\text{H}_2$  at STP = 0.2 g

Mass of copper deposited

Mass of hydrogen

$$= \frac{\text{Eq. mass of copper}}{\text{Eq. mass of hydrogen}}$$

$$\frac{m_{\text{Cu}}}{0.2 \text{ g}} = \frac{63.5 / 2}{1}$$

$$m_{\text{Cu}} = \frac{63.5 \text{ g} \times 0.2}{2} = 6.35 \text{ g.}$$

87.  $\frac{m_{\text{Ni}}}{m_{\text{Cr}}} = \frac{\text{Eq. mass of Ni}}{\text{Eq. mass of Cr}}$

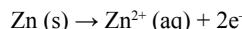
For  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$ , we have

$$\frac{0.3 \text{ g}}{m_{\text{Cr}}} = \frac{59 / 2}{52 / 3}$$

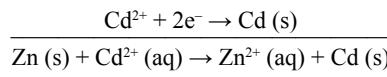
$$m_{\text{Cr}} = 0.3 \text{ g} \times \frac{(52 / 3)}{(59 / 2)} = 0.176 \text{ g}$$

88. Since  $E^\circ_{\text{Cd}^{2+}/\text{Cd}} > E^\circ_{\text{Zn}^{2+}/\text{Zn}}$ , therefore, Zn electrode acts as anode and Cd electrode as cathode.

At anode:



At cathode:



$$Q = [\text{Zn}^{2+}] / [\text{Cd}^{2+}] = 0.004 / 0.2$$

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

$$= -0.403 \text{ V} - (-0.763 \text{ V}) = 0.36 \text{ V}$$

$$E_{\text{cell}} = 0.36 \text{ V} - \frac{0.059}{2} \text{ V} \log_{10} \frac{0.004}{0.2}$$

89.  $2\text{H}^+(1 \text{ M}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}, 100 \text{ atm})$

$$Q = \frac{[\text{H}_2(\text{g})]}{[\text{H}^+]^2} = \frac{100}{(1)^2} = 100$$

$$E_{\text{H}^+/\text{H}_2} = E_{\text{H}^+/\text{H}_2} - \frac{0.059}{2} \text{ V} \log_{10} Q$$

(at 25°C)

$$= 0.0 \text{ V} - \frac{0.059}{2} \text{ V} \log_{10} 100 = -0.059 \text{ V}$$

90.  $Q = I.t = 1.5 \times 7200 = 10800 \text{ C.}$

Atomic wt. of hydrogen is 1 and its valency in water is 1.

Therefore equivalent wt. of hydrogen

$$= \frac{\text{atomic wt.}}{\text{valency}} = \frac{1}{1} = 1$$

A charge of 96500 can produce 1 g of hydrogen

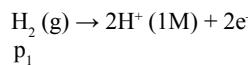
Therefore amount of hydrogen produced by a charge of 10800

$$C = \frac{10800}{96500} = 0.112 \text{ g}$$

Since 2 g of hydrogen molecule at NTP has a volume of 22.4 litres, therefore volume of 0.112 g of hydrogen at NTP is:

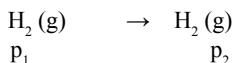
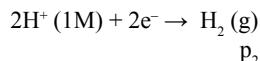
$$\frac{22.4}{2} \times 0.112 = 1.25 \text{ litre.}$$

91. L.H.S half cell:



## 6.58 ■ Electrochemistry

R.H.S half cell:



$$E^\circ_{\text{cell}} = 0.00 \text{ V}, K = \frac{\text{p}_2}{\text{p}_1}, n = 2$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \log e K = 0 - RT \log \frac{\text{p}_2}{\text{p}_1}$$

$$E_{\text{cell}} = \frac{RT}{2F} \log e \frac{\text{p}_1}{\text{p}_2}$$

92.  $c = 0.1 \text{ M}, R = 100 \text{ ohm}, k = 1.29 \text{ ohm}^{-1} \text{ m}^{-1} \frac{1}{a} = k \cdot R = 1.29 \times 100 = 129 \text{ m}^{-1} c = 0.02 \text{ M}, R = 520$

$$\begin{aligned} k &= \frac{1}{R} \times \frac{1}{a} = \frac{1}{320} \times 129 \\ &= 0.248 \text{ ohm}^{-1} \text{ m}^{-1} \end{aligned}$$

$k$  decreases with dilution,

$c = 0.02$  and not 0.2

$$\begin{aligned} \Lambda &= k \times \frac{1}{M \text{ (in m / L)}} \\ &= k \times \frac{1}{M \times 10^3 \text{ (m/m}^3\text{)}} \\ &= \frac{0.248}{0.02 \times 10^3} = 12.4 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1} \\ &= 124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1} \end{aligned}$$

94. Quantity of electricity passed

$$= (4 \text{ A}) \times (30 \times 30 \text{ s}) = 7200 \text{ C}$$



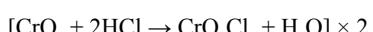
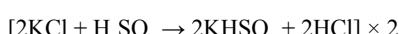
that is,  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

As  $2 \times 96500 \text{ C}$  liberate  $\text{H}_2 = 22.4 \text{ L}$  at STP

So  $7200 \text{ C}$  will liberate

$$\begin{aligned} &= \frac{22.4}{2 \times 96500} \times 7200 \text{ L} \\ &= 0.836 \text{ L.} \end{aligned}$$

95.  $\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{H}_2\text{SO}_4 \rightarrow$



96.  $\Delta G = -n F E_{\text{cell}}$

$$= -2 \times 96500 \times 0.6753 \text{ (at } 25^\circ\text{C)}$$

$$= 130333 \text{ J}$$

$$\Delta S = n F (\partial E / \partial T)_p$$

$$(\partial E / \partial T)_p = \frac{E_2 - E_1}{T_2 - T_1}$$

$$= \frac{0.6753 - 0.6915}{298 - 273} = -6.48 \times 10^{-4}$$

$$\text{So } \Delta S = 2 \times 96500 \times (-6.48 \times 10^{-4})$$

$$= -125.064 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta G = \Delta H - T \Delta S$$

On substituting the values, we have

$$\Delta H = -167.6 \text{ kJ}$$

97. 1 faraday charge liberates 1 eq. of substance.

$$\text{Eq wt. of Al} = 27 / 3 = 9$$

$$\begin{aligned} \text{Number of eq. of Al} &= \frac{\text{wt. of Al}}{\text{Eq. wt.}} \\ &= \frac{4.5}{9} = 0.5 \end{aligned}$$

$$\text{Number of faraday required} = 0.5$$

$$\text{Number of eq. of H}_2 \text{ produce} = 0.5 \text{ eq.}$$

$$\text{Volume occupied by 1 eq. of H}_2$$

$$= \frac{22.4}{2} = 11.2$$

$$\text{volume occupied by 0.5} = 11.2 \times 0.5$$

$$= 5.6 \text{ litre of STP}$$

$$\begin{aligned} 98. E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0591}{2} \log_{10} \frac{1}{[\text{Zn}^{2+}]} \\ &= E^\circ_{\text{cell}} + 0.02955 \log_{10} C \end{aligned}$$

$$E'_{\text{cell}} = E^\circ_{\text{cell}} + 0.02955 \log_{10} \frac{C}{100}$$

$$= E^\circ_{\text{cell}} + 0.02955 \log_{10} C + 0.02955 (-2)$$

$$\text{So } E_{\text{cell}} \text{ will decrease by } 0.02955 \times 2 \text{ V}$$

$$= 0.059 \text{ V} = 59 \text{ mV.}$$

99. EMF for the cell,  $\text{Zn} | \text{Zn}^{2+} \parallel \text{Cu}^{2+} | \text{Cu}$

$$= 0.34 - (-0.76) = 1.10 \text{ V.}$$

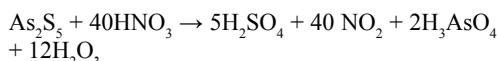
EMF for the cell,  $\text{Fe} | \text{Fe}^{2+} \parallel \text{Cu}^{2+} | \text{Cu}$

$$= 0.34 - (-0.41) = 0.75 \text{ V}$$

As the two cells are connected in series, therefore then net EMF of the two cells

$$= 1.10 + 0.75 = 1.85 \text{ V}$$

100. The balanced equation is,



Thus, the value of x and y are 40 and 40.

102. For a cell reaction in equilibrium at 298 K.

$$E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \times \log_{10} K_c$$

$$0.46 = \frac{0.0591}{2} \times \log_{10} K_c$$

$$\log_{10} K_c = \frac{2 \times 0.46}{0.0591} = 15.57$$

$$K_c = 3.7 \times 10^{15} = 4 \times 10^{15}$$

103. The reduction potential of Zn, Cu, Ag and Ni (obtained by reversing the sign of oxidation potentials) are  $-0.76$ ,  $+0.34$ ,  $+0.80$  and  $-0.25$  respectively.

The maximum EMF of the cell is obtained when the electrode potential of the anode is minimum and that of the cathode is maximum, that is, Zn and Ag respectively.

$$\text{EMF} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$= +0.80 - (-0.76) = +1.56 \text{ V.}$$

104.  $E = 0.77 - \frac{0.0591}{1} \log_{10} \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$

$$= 0.77 - 0.059 \log_{10} \frac{1.2}{0.012}$$

$$= 0.77 - 0.118 = 0.652 \text{ V}$$

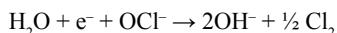
105. (i)  $\text{H}_2\text{O} + \text{OCl}^- + 2e^- \rightarrow \text{Cl}^- + 2\text{OH}^-$

$$E^{\circ} = 0.94 \text{ V}$$

(ii)  $\frac{1}{2}\text{Cl}_2 + e^- \rightarrow \text{Cl}^-;$

$$E^{\circ} = 1.36 \text{ V}$$

On subtracting equation (ii) from equation (i), we get



$$E^{\circ} = 0.94 - 1.36 = -0.42 \text{ V.}$$

106.  $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log_{10} Q$

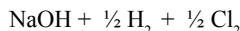
Here  $Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$

For complete discharge  $E_{\text{cell}} = 0$ .

$$\text{So } E_{\text{cell}}^{\circ} = \frac{0.0591}{2} \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 10^{37.3}$$

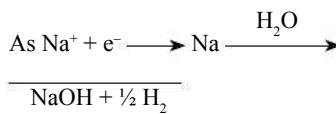
107.  $\text{NaCl} + \text{H}_2\text{O}$  Electrolysis



At anode At cathode

400 ml of 1 M NaCl solution contains NaCl

$$= \frac{1}{1000} \times 400 \text{ mol} = 0.4 \text{ mol}$$



As 1 F produces 1 mol of NaOH

$$\text{So } 0.04 \text{ F produces NaOH} = 0.04 \text{ mol}$$

Thus, 400 ml of the solution now contain 0.04 mol of NaOH.

Molar concentration of NaOH solution

$$= \frac{0.04}{400} \times 1000 = 0.1 \text{ M}$$

$$[\text{OH}^-] = 0.1 \text{ M}$$

$$[\text{H}^+] = 10^{-13} \text{ M}$$

$$\text{So pH} = 13.$$

108.  $k = G \times G^* = \frac{1}{R} \times G^*$

$$= \frac{1}{2.5 \times 10^3 \Omega} \times 1.25 \text{ cm}^{-1}$$

$$= 5 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$$

$$\Lambda_{\text{eq}} = \frac{1000 \text{ K}}{\text{Normality}}.$$

$$= \frac{1000 \times 5 \times 10^{-4}}{0.1 \text{ N}}$$

$$= 5.0 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

109.  $\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$

As 1 mol i.e. 40 g Ca is deposited by 2 F, i.e.  $2 \times 96500 \text{ C}$

So 60 g Ca will be deposited by

$$= \frac{2 \times 96500}{40} \times 60 \text{ C} = 289500 \text{ C}$$

## 6.60 ■ Electrochemistry

As  $Q = I \times t$

$$t = \frac{289500}{5} \text{ s} = 57900 \text{ s}$$

$$= \frac{57900}{60 \times 60} \text{ hrs} = 16 \text{ hours}$$

110. The cell reaction is



$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303 \text{ RT}}{2F} \log_{10} \frac{1}{[\text{Ag}^+]^2}$$

$$0.62 = 0.80 + 0.06 \log_{10} [\text{Ag}^+]$$

$$\log_{10} [\text{Ag}^+] = \frac{-0.18}{0.06} = -3$$

$$[\text{Ag}^+] = \text{antilog}(-3) = 1.0 \times 10^{-3} \text{ M}$$

$$= (1.0 \times 10^{-3}) \times 108 \text{ g L}^{-1}$$

$$= 0.108 \text{ g L}^{-1}$$

Amount of Ag present in 100 ml solution

$$= 0.0108 \text{ g}$$

$$\text{So \% of Ag} = \frac{0.0108}{108} \times 100 = 1 \%$$

112.  $Q = I.t = 2 \times 1800 = 3600 \text{ C.}$

Atomic wt. of chlorine is 35.5 and its valency in NaCl is 1.

Therefore equivalent weight of chlorine

$$\frac{\text{Atomic wt.}}{\text{Valency}} = \frac{35.5}{1} = 35.5$$

96500 of charge evolves 35.5 g of chlorine

Therefore amount of chlorine evolved by a charge of 3600

$$C = \frac{35.5}{96500} \times 3600 = 1.32 \text{ g}$$

113.  $\text{S}_2\text{O}_6^{2-} = +5$

So increasing order of oxidation state of 'S' is



114. As the balanced equation is



So for it a = 5, b = 6, c = 3 and d = 3

115.  $\frac{\text{Wt. of Cu deposited}}{\text{Wt. of H}_2 \text{ produced}}$

$$= \frac{\text{eq. wt. of Cu}}{\text{eq. et. of H}} = \frac{64/2}{1}$$

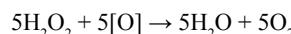
$$\frac{0.16}{\text{wt. of H}_2} = \frac{32}{1}$$

$$\text{wt. of H}_2 = 0.16 / 32 = 5 \times 10^{-3} \text{ g}$$

volume of  $\text{H}_2$  liberated at STP

$$= \frac{22400}{2} \times 5 \times 10^{-3} \text{ cc} = 56 \text{ cc}$$

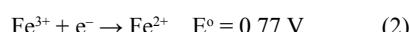
116.  $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow$



As 5 moles of  $\text{H}_2\text{O}_2$  are required to reduce 2 moles of  $\text{KMnO}_4$ .

So  $5/2$  moles of  $\text{H}_2\text{O}_2$  are required per mole of  $\text{KMnO}_4$ .

117.  $\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe} \quad E^{\circ} = -0.44 \text{ V} \quad \dots\dots(1)$



Adding equations (1) and (2)



$$E_1^{\circ} + E_2^{\circ} = -0.88 + 0.77 = -0.11 \text{ V}$$

$$n = 3$$

$$E_3^{\circ} = \frac{-0.11}{3} = -0.037 \text{ V}$$

118.  $E^{\circ}$  for the given reaction

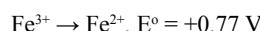
$$= 0.855 - 0.799 = 0.056 \text{ V}$$

$$E_{\text{cell}}^{\circ} = \frac{0.0591}{2} \log_{10} K_C$$

$$\log_{10} K_C = \frac{0.056 \times 2}{0.059} = 1.8983$$

$$K_C = \text{Antilog } 1.8983 = 79.12 \approx 79$$

119.  $[\text{Fe}(\text{CN})_6]^{3-} \rightarrow [\text{Fe}(\text{CN})_6]^{4-}, E^{\circ} = +0.35 \text{ V}$



Higher the positive reduction potential, stronger is the oxidizing agent. Oxidising agent oxidizes other compounds and gets itself reduced easily.

121. Oxidation number of oxygen in  $\text{OF}_2$

$$\Rightarrow x + (-2) = 0 \Rightarrow x = +2$$

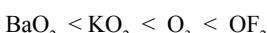
Oxidation number of oxygen in  $\text{KO}_2$

$$\Rightarrow (+1) + 2x = 0 \Rightarrow x = -1/2$$

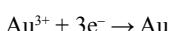
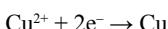
Oxidation number of oxygen in  $\text{BaO}_2$

$$\Rightarrow (+2) + 2x = 0 \Rightarrow x = -1$$

As, Correct order is



122.  $\text{Ag}^+ + e^- \rightarrow \text{Ag}$ ,



3F will deposit 3 moles of Ag, 3/2 moles of Cu and 1 mole of Au.

So Molar ratio = 3 : 3/2 : 1 = 6 : 3 : 2

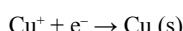
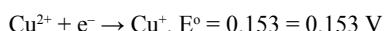
123.  $\text{H}^+ + e^- \rightarrow \frac{1}{2} \text{H}_2$ ,

$$E = E^\circ - \frac{0.0591}{n} \log_{10} \frac{1}{[\text{H}^+]}$$

$$= 0 - \frac{0.0591}{1} \text{ pH}$$

$$= -0.0591 \times 3 = -0.177 \text{ V}$$

126.  $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} (\text{s})$ ,  $E^\circ = 0.33 = -0.66 \text{ F}$

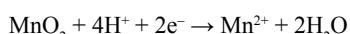


$$-\Delta G^\circ_3 = \Delta G_2 + \Delta G_1$$

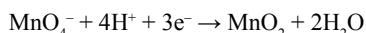
$$= +0.153 \text{ F} - 0.66 \text{ F} = 0.507$$

131.  $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$

$$\Delta G^\circ = -5 \times 1.51 \text{ F}$$



$$\Delta G^\circ = -2 \times 1.23 \text{ F}$$



$$\Delta G^\circ = (-7.55 \text{ F} + 2.46 \text{ F}) = -5.09 \text{ F}$$

$$E^\circ \text{MnO}_4^- / \text{MnO}_2 = \frac{-5.09 \text{ F}}{-3\text{F}} = +1.696 \text{ V.}$$

133.  $E = E^\circ - 0.059 \log [\text{H}^+]^2$

$$= 1.30 - \frac{0.059}{2} \log (10^{-2})^2$$

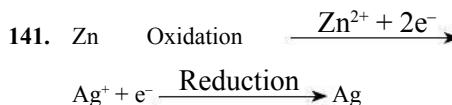
$$= 1.30 + \frac{0.236}{2} = 1.418 \text{ V}$$

### Multiple Correct Answer Type Questions

136. As only Oxidation takes place at anode and  $\text{Cr}^{3+}$  is not oxidized to  $\text{Cr}_2\text{O}_7^{2-}$  under given condition.

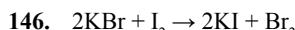
137. As specific conductance decreases with dilution, whereas the equivalent conductance increases with dilution and conductance of all electrolytes increase with temperature as the ions move faster at higher temperature .

140. As  $\Delta G_f^\circ$  for most of the sulphides are more than those of  $\text{CS}_2$  and  $\text{H}_2\text{S}$  so carbon and hydrogen can not reduced metal sulphides into metal.

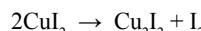


142. In an electrochemical cell, oxidation takes place at the anode and reduction takes place at the cathode.

Therefore  $\text{H}_2$  is anode and Cu is cathode.

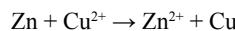


As this reaction is not possible because  $\text{Br}^-$  ion is not oxidized in  $\text{Br}_2$  with  $\text{I}_2$  due to higher electrode potential of  $\text{I}_2$  than bromine.



so  $\text{CuI}_2$  is not formed.

149. In Daniel cell the cell reaction is,



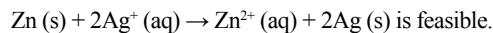
So  $\text{Cu}^{2+}$  ions (cations) move towards Cu electrode (cathode) and get accumulated as Cu metal.

152. Standard emf of the cell ( $E^\circ_{\text{cell}}$ )

$$= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$= 0.80 - (-0.76) = 1.56 \text{ V.}$$

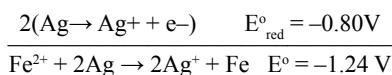
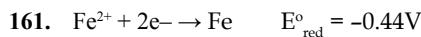
as emf is +ve, therefore the cell reaction



- is feasible.  
153. As reduction occurs at Ag electrode, so increase in the concentration of  $\text{Ag}^+$  or decreases in concentration of  $\text{Cu}^{2+}$  will increases the voltage.

157. As For a galvanic cell under equilibrium condition,

$$E_{\text{cell}} = 0.$$

**Comprehensions**


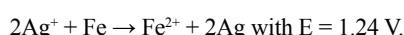
162. E for the reaction is calculated using the Nernst equation:

$$E = E^\circ - \left( \frac{0.0592 \text{ V}}{2} \right) \log \frac{[\text{Ag}^+]^2}{[\text{Fe}^{2+}]}$$

$$= -1.24 \text{ V} - (-0.0296 \text{ V}) \log \frac{(0.0100)^2}{(0.100)}$$

$$= -1.24 \text{ V} - (-0.887 \text{ V}) = -1.15 \text{ V}$$

163. The reaction that is spontaneous is



$$W_{\text{max}} = -nFE = -(2 \text{ mole}^-)$$

$$\left( \frac{96.500 \text{ C}}{1 \text{ mole}} \right) (1.24 \text{ V}) \frac{1\text{J}}{1\text{C} - \text{V}}$$

$$= -2.39 \times 10^5 \text{ J}$$

or in kwh ,

$$(2.39 \times 10^5 \text{ J}) \left( \frac{1 \text{ kwh}}{3.6 \times 10^6 \text{ J}} \right)$$

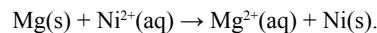
$$= 6.6 \times 10^{-2} \text{ kwh}$$

164. The half- reaction with the most negative standard potential becomes the oxidation half-reaction.

$$E^\circ = E^\circ_{\text{(cathode)}} - E^\circ_{\text{(anode)}} = -0.28 \text{ V} - (-0.237 \text{ V})$$

$$= 2.09 \text{ V.}$$

The overall reaction is



165. The Nernst equation is used to solve for the cell potential. Note that two moles of electrons are transferred in the reaction.

$$E = \frac{2.09 \text{ V}}{2} - 0.5092 \text{ V} \log \frac{0.50}{1.0}$$

$$= 2.10 \text{ V}$$

166.  $\log K = \frac{nE^\circ}{0.0592} = \frac{(2.09)}{0.0592} = 70.6$

$$K = 10^{70.6} = 4 \times 10^{70}$$

167.  $E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} - \frac{0.0591}{6}$

$$\times \left( \frac{\log [\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}]} \times \frac{1}{[\text{H}^{+}]^{14}} \right)$$

$$E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 - \frac{0.0591}{6} \log \frac{1}{(0.01)^{14}}$$

On solving we get  $E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.0542 \text{ V}$

169. As  $\Delta G = \Delta G^\circ + RT \ln Q$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$\text{So } \Delta G = -nFE^\circ + 2.303 RT \log \frac{[\text{Cr}^{3+}]}{[\text{Ag}^+]^3}$$

On solving

$$\Delta G = -422838.3 \text{ J or } -422.83 \text{ kJ}$$

170.  $E^\circ_{\text{cell}} = 0.06 (3 - 4) = -0.06 \text{ V}$

$$E_{\text{cell}} = E^\circ_{\text{H}^+/\text{H}_2} - E^\circ_{\text{OH}^-/\text{Cd(OH)}_2\text{Cd}}$$

$$= E^\circ_{\text{H}^+/ \text{H}^-} - E^\circ_{\text{cd}^{2+}/\text{Cd}}$$

$$\text{i.e. } E_{\text{cell}} = E^\circ - \frac{0.06}{2} \log \frac{[\text{Cd}^{2+}]}{[\text{H}^+]^2}$$

As  $E_{\text{cell}} = 0$ ,

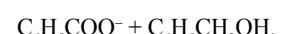
$$\text{So } E^\circ_{\text{cell}} = 0.03 \log \times \frac{[\text{Cd}^{2+}][\text{OH}^-]^2}{K_w^2}$$

$$\log \frac{K_{\text{sp}}}{K_w^2} = \frac{0.39}{0.03} = 13$$

On taking antilog

$$K_{\text{sp}} = 10^{13} \times (10^{-14})^2 = 10^{-15}$$

171. In  $\text{Cl}_2 + \text{OH}^- \rightarrow \text{ClO}^- + \text{Cl}^- + \text{H}_2\text{O}$ , the oxidation number of Cl increases from 0 to +1 and decreases from 0 to -1.



$\text{C}_6\text{H}_5\text{CHO}$  is oxidized to  $\text{C}_6\text{H}_5\text{COO}^-$  and at the same time reduced to  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  (Cannizaro reaction).

173.  $\text{MnO}_4^- + \text{I}_2 \rightarrow \text{Mn}^{2+} + 2\text{IO}_3^- + \dots$

O.N. of Mn : decrease = 5

O.N. of I : increase = 5 for one I atom and 10 for two I atoms

Molar ratio,  $\text{MnO}_4^- : \text{I}_2 = 2 : 1$

175.  $E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K$

$$(0.8 - 0.05) = \frac{1}{2} \times \frac{0.0592}{2.303} \ln K$$

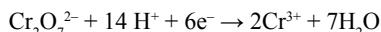
$$\ln K = \frac{(0.8 - 0.05) \times 2 \times 2.303}{0.0592} = 58.38$$

176. On increasing concentration of  $\text{NH}_3$ , the concentration of  $\text{H}^+$  ion decreases. Therefore Ered increases.

178. Reduction potential of  $\text{I}_2$  is less than  $\text{Cl}_2$ .

179. Reaction of  $\text{Mn}^{3+}$  with  $\text{H}_2\text{O}$  is spontaneous.

187. A and R both are false.



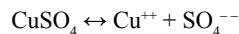
(in acidic medium)

$$\text{so equivalent weight} = \frac{\text{mol. wt.}}{6}$$

$$= \frac{294}{6} = 49.0$$

188. For a strong electrolyte the plot of molar conductivity ( $\Lambda_m$ ) against  $\sqrt{c}$  is nearly linear.

197. During electrolysis,  $\text{CuSO}_4$  converted into  $\text{Cu}^{++}$

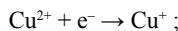


### The IIT-JEE Corner

212. (i)  $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ ;

$$\text{as } \Delta G_1^\circ = -nFE^\circ = -2F \times 0.337$$

for the process (ii)



$$\Delta G_2^\circ = -1F \times 0.153$$

now subtract eq. (ii) from (i)



$$= -0.674 \text{ F} - (-0.153 \text{ F})$$

$$= -0.674 \text{ F} + 0.153 \text{ F}$$

$$= -0.521 \text{ F}$$

$$\text{Now } -nFE^\circ_{\text{Cu}^{2+}/\text{Cu}} = -0.521 \text{ F}$$

$$E^\circ_{\text{Cu}^{2+}/\text{Cu}} = -0.521 \text{ V.}$$

213. Lower the reduction potential, stronger is the reducing agent.

214. Higher the reduction potential, better the oxidizing agent. Since the R.P. of Y is greater.

than X but less than Z, hence, Y will oxidize X but not Z.

215. (0)  
 $\text{S}_8$  elemental state

$x = -1$



$$2x - 2 = 0$$

$$2x = 2 \text{ so } x = 1$$

$+1 \ x$



$$x + 2 = 0$$

$$x = -2$$

216.  $\text{M}^+ + e^- \rightarrow \text{M} ; E^\circ = + 0.44 \text{ V}$

$\text{X} + e^- \rightarrow \text{X}^- ; E^\circ = + 0.33 \text{ V}$

Now in case of b.

$$E_{\text{mf}}^\circ = E^\circ c - E^\circ a$$

$$= E^\circ \text{ M}^+ / \text{M} - E^\circ \text{ X}^- / \text{X}^-$$

$$= 0.44 - 0.33 = 0.11 \text{ V}$$

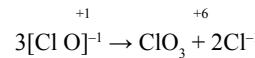
Thus  $\text{M}^+ + \text{X}^- \rightarrow \text{M} + \text{X}$  is a spontaneous reaction.

217.



218. Ionic mobilities (or transport numbers) of  $\text{K}^+\text{NO}_3^-$  are nearly same.

219.



This is an example of disproportionation reaction.

220. Since the ionic character decreases in the order  $\text{KCl} > \text{NaCl} > \text{LiCl}$

221.  $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

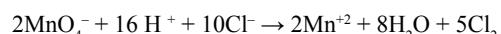
Since  $\text{K}_2\text{Cr}_2\text{O}_7$  accepts 6 electrons for its reduction to  $\text{Cr}^{3+}$  ions.

$$\text{Eq. wt.} = \frac{\text{Mol. wt.}}{6}$$

222. When  $\text{MnO}_4^-$  is used in aqueous HCl,  $\text{MnO}_2$  reacts with  $\text{Fe}^{+2}$  as well as with HCl as explained below:



$$E^\circ_{\text{cell}} = 1.51 - 0.77 = 0.74 > 0$$

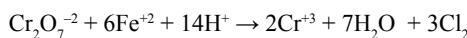


$$E^\circ_{\text{cell}} = 1.51 - 0.77 = 0.74 > 0$$

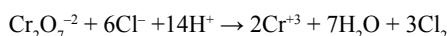
As such  $\text{MnO}_4^-$  cannot be used for the quantitative estimation of aqueous  $\text{Fe}(\text{NO}_3)_2$ . Thus option A is

## 6.64 ■ Electrochemistry

not correct. Similarly, we can show that  $\text{Cr}_2\text{O}_7^{2-}$  will react with  $\text{Fe}^{2+}$  but not with  $\text{HCl}$ .



$$E^\circ_{\text{cell}} = 1.38 - 0.77 = 0.61 \text{ V} > 0$$



$$E^\circ_{\text{cell}} = 1.38 - 1.40 = -0.02 \text{ V} < 0$$

Thus, the second reaction is not possible. Thus  $\text{Cr}_2\text{O}_7^{2-}$  in aqueous  $\text{HCl}$  can be used for the quantitative estimation of aqueous  $\text{Fe}(\text{NO}_3)_2$ .

Option (C) and (D) are correct.

- 223.** In an electrolytic cell, electrons do not flow themselves. It is the migration of ions towards oppositely charged electrodes that indirectly constitutes the flow of electrons from cathode to anode through internal supply.
- 224.** The maximum O.S. of Cr is +6 in  $\text{CrO}_2\text{Cl}_2$  and that of Mn is +7 in  $\text{MnO}_4^-$ .



$$E = E^\circ - \frac{0.0591}{n} \log K_c$$

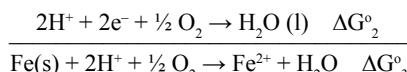
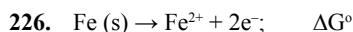
$$0.0295 = E^\circ - \frac{0.0591}{2} \log \frac{0.01}{0.001}$$

$$E^\circ = 0.2905 + 0.0295 = 0.32 \text{ volt}$$

$$E^\circ = \frac{0.0591}{n} \log K_{\text{eq}}$$

$$0.32 = \frac{0.0591}{2} \log K_{\text{eq}} = 0.02945 \log K_{\text{eq}}$$

$$K_{\text{eq}} = 10^{0.32/0.0295}$$



$$\Delta G^\circ_2 + \Delta G^\circ_1 = \Delta G^\circ_3$$

$$\Delta G^\circ_3 = (-2F \times 0.44) + (-2F \times 1.23)$$

$$= -(2 \times 96500 \times 0.44 + 2 \times 96500 \times 1.23)$$

$$= -322310 \text{ J} = -322 \text{ kJ.}$$

- 227.** The solubility of  $\text{AgBr}$  in presence of  $10^{-7}$  molar  $\text{AgNO}_3$  is  $3 \times 10^{-7} \text{ M}$ .

$$\text{Therefore } [\text{Br}^-] = 3 \times 10^{-4} \text{ m}^3,$$

$$[\text{Ag}^+] = 4 \times 10^{-4} \text{ m}^3 \text{ and } [\text{NO}_3^-] = 10^{-4} \text{ m}^3$$

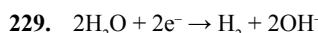
$$\text{Therefore } K_{\text{total}} = \text{KBr} + \text{KAg}^+ + \text{KNO}_3^- = 55 \text{ Sm}^{-1}$$



n factor of  $\text{Cr}_2\text{O}_7^{2-} = 6$

n factor of  $\text{Fe}^{2+} = 1$

So to reduce one mole of dichromate 6 moles of  $\text{Fe}^{2+}$  are required



For 0.01 mole  $\text{H}_2$  0.02 mole of  $\text{e}^-$ s are consumed

Charge required =  $0.02 \times 96500 \text{ C} = i \times t$

$$\text{Time required} = \frac{0.02 \times 96500}{10 \times 10^{-3}}$$

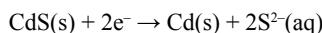
$$= 19.3 \times 10^4 \text{ sec}$$

## Numericals For Practice

- 1.** Given the following standard potentials at  $25^\circ\text{C}$ :



$$E^\circ = -0.403 \text{ V}$$



$$E^\circ = -1.21 \text{ V}$$

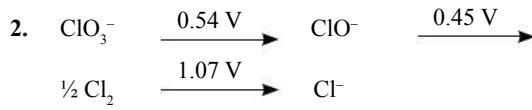
Calculate  $K_{\text{sp}}$  for  $\text{CdS}$

a.  $1 \times 10^{-25}$

b.  $1 \times 10^{-27}$

c.  $1 \times 10^{27}$

d.  $1 \times 10^{-29}$



If  $E^\circ$  for the conversion of  $\text{ClO}^-$  to  $\text{Cl}^-$  is 0.71 and that of  $\text{ClO}_3^-$  to  $\text{Cl}^-$  is X find the value of X?

a. 0.3

b. 0.5507

c. 0.6

d. 0.06

- 3.** Given  $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.72 \text{ V}$ ,  $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.42 \text{ V}$ . The potential for the cell

- $\text{Cr} | \text{Cr}^{3+} (0.1 \text{ M}) \parallel \text{Fe}^{2+} (0.01 \text{ M}) | \text{Fe}$  is
- 0.26 V
  - 0.399 V
  - 0.339 V
  - 0.26 V
4. An electric current of 1 A is passed through acidulated water for 160 minutes and 50 seconds. What is the volume of the oxygen liberated at the anode (as reduced to NTP)?
- 2.24 litre
  - 22.4 litre
  - 1.12 litre
  - 11.2 litre
5.  $E_{\text{Cu}^{2+}/\text{Cu}^+}^\circ = 0.153 \text{ V}$ ;  $E_{\text{Cu}^{2+}/\text{Cu}}^\circ = 0.337 \text{ V}$ .  $E_{\text{Cu}^+/ \text{Cu}}^\circ$  is
- 0.495 V
  - 0.521 V
  - 0.186 V
  - 0.369 V
6. A voltaic cell is constructed that is based on the following reaction:
- $$\text{Sn}^{2+} (\text{aq}) + \text{Pb}(\text{s}) \rightarrow \text{Sn}(\text{s}) + \text{Pb}^{2+} (\text{aq})$$
- If the concentration of  $\text{Sn}^{2+}$  in the cathode compartment is 1.00 M and the cell generates an emf of +0.22 V, what is the concentration of  $\text{Pb}^{2+}$  in the anode compartment?
- $2 \times 10^{-8} \text{ M}$
  - $2 \times 10^8 \text{ M}$
  - $2 \times 10^{-6} \text{ M}$
  - $2 \times 10^{-6} \text{ M}$
7. If in the above problem the anode compartment contains  $[\text{SO}_4^{2-}] = 1.00 \text{ M}$  in equilibrium with  $\text{PbSO}_4(\text{s})$ , what is the  $K_{\text{sp}}$  of  $\text{PbSO}_4$ ?
- $3.4 \times 10^{-8}$
  - $1.7 \times 10^8$
  - $3.4 \times 10^8$
  - $1.7 \times 10^{-8}$
8. A graph is plotted between  $E_{\text{cell}}^\circ$  of quinhydrone half cell and pH of solution. Intercept is 0.698 V. At what pH,  $E_{\text{cell}}^\circ$  will become 0.491 V?
- 1.75
  - 3.5
  - 4.5
  - 11.5
9. Given that  $K = 3.76 \times 10^{14}$  for the reaction  $2\text{Fe}^{3+}(\text{aq}) + \text{Cu}(\text{s}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{Cu}^{2+}(\text{aq})$
- at 25°C, which of the following corresponds to  $E^\circ$  for the reaction?
- 0.43 V
  - 0.22 V
  - 0.43 V
  - 0.22 V
10. Calculate the cell EMF in mV for  $\text{Pt} | \text{H}_2 (1 \text{ atm}) | \text{HCl} (0.01 \text{ M}) | \text{AgCl}(\text{s}) | \text{Ag}(\text{s})$  at 298 K. If  $\Delta G^\circ_f$  values are at 25°C -109.56 kJ/mol for  $\text{AgCl}(\text{s})$  and -130.79 kJ/mol for  $(\text{H}^+ + \text{Cl}^-)(\text{aq})$
- 228 mV
  - 45.6 mV
  - 654 mV
  - 456 mV

11. Using standard cell potentials, calculate  $\Delta G^\circ$  for the reaction  $5\text{AgI}(\text{s}) + \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) \rightarrow 5\text{Ag}(\text{s}) + 5\text{I}^-(\text{aq}) + \text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq})$
- 160 kJ
  - 801 kJ
  - 160 kJ
  - 801 kJ
12. What is the electrode potential at 25°C for the reaction  $\text{Cd}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Cd}^{2+}(\text{aq}) + \text{H}_2(\text{g})$  when the concentrations are:  
 $\text{Cd}^{2+}(\text{aq}) = 0.100 \text{ M}$ ;  $P_{\text{H}_2} = 2.00 \text{ atm}$ ; and  $\text{H}^+ = 0.200 \text{ M}$ ?
- 0.283 V
  - 0.365 V
  - 0.382 V
  - 0.424 V
13. At 298 K a cell reaction exhibits a standard emf of +0.17 V. The equilibrium constant for the cell reaction is  $5.5 \times 10^5$ . What is the value of n for the cell reaction?
- 4
  - 2
  - 6
  - 1
14. How long does it take to plate on to a surface 1.00 g of chromium metal using a current of 3.00 amperes? ( $1\text{F} = 96,500$  coulombs) give this half-reaction
- $3.71 \times 10^3 \text{ s}$
  - $1.36 \times 10^3 \text{ s}$
  - $6.17 \times 10^2 \text{ s}$
  - $3.71 \times 10^{-3} \text{ s}$
15. The mass of copper deposited from a solution of  $\text{Cu}_2\text{S}$  by passing a current of 2.5 ampere for 6 minute is
- 0.6 g
  - 0.7 g
  - 0.5 g
  - 0.9 g
16. In the electrolysis of aqueous NaCl, how many liters of  $\text{Cl}_2(\text{g})$  (at STP) are generated by a current of 16.8 A for a period of 90.0 min?
- 21.0 L  $\text{Cl}_2$
  - 10.5 L  $\text{Cl}_2$
  - 5.2 L  $\text{Cl}_2$
  - 20.5 L  $\text{Cl}_2$
17. The reduction potential of a hydrogen electrode at pH = 10, at 298 K is
- 0.591 V
  - zero
  - +0.591 V
  - 0.0591 V
18. How many atoms of calcium will be deposited from a solution of  $\text{CaCl}_2$  by a current of 25 milliamperes flowing for 60 s?
- $4.7 \times 10^{17}$
  - $4.7 \times 10^{18}$
  - $4.7 \times 10^9$
  - $4.7 \times 10^{12}$
19. The standard potential for the reduction of  $\text{AgSCN}(\text{s})$  is +0.0895 V:
- $$\text{AgSCN}(\text{s}) \text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{SCN}^-(\text{aq})$$

## 6.66 ■ Electrochemistry

Using this value and the electrode potential for  $\text{Ag}^+(\text{aq})$ , calculate the  $K_{\text{sp}}$  for  $\text{AgSCN}$ .

- a.  $1 \times 10^{12}$
- b.  $2 \times 10^{-12}$
- c.  $1 \times 10^{-12}$
- d.  $2 \times 10^{12}$

20. At  $25^\circ\text{C}$ , electrode potential of  $\text{Mg}^{2+}/\text{Mg}$  electrode in which concentration of  $\text{Mg}^{2+}$  ions is  $0.1 \text{ M}$  ( $E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.36 \text{ V}$ )

- a.  $-2.36 \text{ V}$
- b.  $-2.39 \text{ V}$
- c.  $-4.75 \text{ V}$
- d.  $-3.95 \text{ V}$

21. Find the oxidizing power of  $(1 \text{ M}, \text{MnO}_4^-/\text{Mn}^{2+}, 1\text{M})$  couple decreased if the  $\text{H}^+$  concentration is decreased from  $1\text{M}$  to  $10^{-4}\text{M}$  at  $25^\circ\text{C}$ ?

- a.  $0.38 \text{ V}$
- b.  $-0.38 \text{ V}$
- c.  $-0.19$
- d.  $-0.76$

22. A cell reaction is given by  $\text{A} + \text{B}^{2+}(\text{aq}) \rightarrow \text{C} + \text{D}^{2+}(\text{aq})$ . If its equilibrium constant ( $K_c$ ) is 100, what is the value of  $E^\circ_{\text{cell}}$  at  $25^\circ\text{C}$ ?

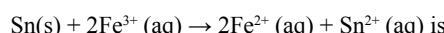
- a.  $0.0591$
- b.  $0.1283$
- c.  $0.0356$
- d.  $0.2366$

23. Consider the following  $E^\circ$  values

$$E_{(\text{Fe}^{3+}/\text{Fe}^{2+})} = +0.77 \text{ V}$$

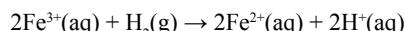
$$E_{(\text{Sn}^{2+}/\text{Sn})} = -0.14 \text{ V}$$

Under standard conditions the potential for the reaction



- a.  $1.68 \text{ V}$
- b.  $0.91 \text{ V}$
- c.  $0.63 \text{ V}$
- d.  $1.46 \text{ V}$

24. A voltaic cell utilizes the following reaction and operates at  $20^\circ\text{C}$ :



What is the emf of this cell under standard conditions?

- a.  $1.572 \text{ V}$
- b.  $0.771 \text{ V}$
- c.  $0.385 \text{ V}$
- d.  $0.762 \text{ V}$

25. In the above problem : What is the emf for this cell when  $[\text{Fe}^{3+}] = 0.50 \text{ M}$ ,  $P_{\text{H}_2} = 0.25 \text{ atm}$ ,  $[\text{Fe}^{2+}] = 0.010 \text{ M}$ , and the pH in both compartments is 4.00

- a.  $2.182 \text{ V}$
- b.  $10.91 \text{ V}$
- c.  $1.091 \text{ V}$
- d.  $21.82 \text{ V}$

26. In a half-cell containing  $[\text{Tl}^{3+}] = 0.2 \text{ M}$  and  $[\text{Tl}^+] = 0.02 \text{ M}$ , the cell potential is  $-1.2495 \text{ V}$  for the reaction  $\text{Tl}^+ \rightarrow \text{Tl}^{3+} + 2\text{e}^-$ . The standard reduction potential of the  $\text{Tl}^+/\text{Tl}^{3+}$  couple at  $25^\circ\text{C}$  is

- a.  $1.22 \text{ V}$
- b.  $1.44 \text{ V}$
- c.  $0.61 \text{ V}$
- d.  $2.44 \text{ V}$

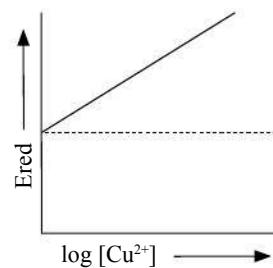
27. For the following cell  $\text{Pb} \mid \text{PbCl}_2(\text{s}) \mid \text{PbCl}_2(\text{soln.}) \mid \text{AgCl}(\text{s}) \mid \text{Ag}$  the potential at  $298 \text{ K}$  is  $0.490 \text{ V}$  and the variation of emf with temperature is given by  $E = a - (1.86 \times 10^{-4} \text{ V K}^{-1})(T - 25 \text{ K})$ . Calculate  $\Delta G$ .

- a.  $47.28 \text{ Kcal}$
- b.  $-94.57 \text{ K.cal}$
- c.  $-47.28 \text{ Kcal}$
- d.  $94.57 \text{ K.cal}$

28. The standard emf of a cell, involving one electron change is found to be  $0.591 \text{ V}$  at  $25^\circ\text{C}$ . The equilibrium constant of the reaction is ( $F = 96500 \text{ C mol}^{-1}$ ,  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ )

- a.  $1.0 \times 10^{30}$
- b.  $1.0 \times 10^1$
- c.  $1.0 \times 10^5$
- d.  $1.0 \times 10^{10}$

29.  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ ;  $\log [\text{Cu}^{2+}]$  vs  $E_{\text{red}}$  graph is given below  $OA = 0.34 \text{ V}$  then electrode potential of the half cell of  $\text{Cu} \mid \text{Cu}^{2+}(0.1 \text{ M})$  will be :



- a.  $-0.34 + \frac{0.0591}{2} \text{ V}$
- b.  $0.34 + \frac{0.0591}{2} \text{ V}$
- c.  $0.34 \text{ V}$
- d.  $-0.34 \text{ V}$

30. Electrolysis of a solution of  $\text{HSO}_4^-$  ions produces  $\text{S}_2\text{O}_8^{2-}$ . Assuming 75 % current efficiency, what current must be employed to achieve a production rate of 1 mole of  $\text{S}_2\text{O}_8^{2-}$  per hour?

- a.  $7.14 \text{ amp}$
- b.  $35.75 \text{ amp}$
- c.  $71.5 \text{ amp}$
- d.  $142.85 \text{ amp}$

31. The emf of a cell corresponding to the reaction  $\text{Zn}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Zn}^{2+} + \text{H}_2(\text{g})$  ( $0.1 \text{ M}$ ) ( $1 \text{ atm}$ )

is  $0.28 \text{ V}$  at  $25^\circ\text{C}$  and  $E^\circ_{\text{Zn/Zn}^{2+}} = 0.76 \text{ V}$  find the pH of the solution at H electrode.

- a.  $8.635$
- b.  $5.365$
- c.  $6.365$
- d.  $4.617$

32. From the following standard electrode potentials at  $25^\circ\text{C}$

$$\text{Cu}^{2+} + 2\text{e}^- = \text{Cu} ; \quad E^\circ = +0.34 \text{ V}$$

$$\text{Cu}^{2+} + \text{e}^- = \text{Cu}^+ ; \quad E^\circ = +0.15 \text{ V}$$

Calculate equilibrium constant of the reaction  $\text{Cu} + \text{Cu}^{2+} \rightarrow 2\text{Cu}^+$ .

- a.  $3.72 \times 10^{-5}$       b.  $3.72 \times 10^7$   
 c.  $3.72 \times 10^{-7}$       d.  $3.72 \times 10^5$
33. Calculate the equilibrium constant at 298 K for the disproportionation of 3 mole of aqueous  $\text{HNO}_2$  to yield NO and  $\text{NO}_3^-$  ions. The  $E^\circ$  for reduction of  $\text{HNO}_2$  to NO is 0.98 V and  $E^\circ$  for reduction of  $\text{NO}_3^-$  to  $\text{HNO}_2$  is 0.95 V  
 a. 53.49      b. 40.53  
 c. 49.53      d. 42.53

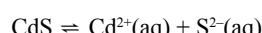
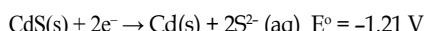
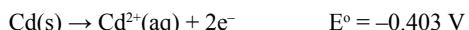
34. The specific conductance of 0.01 M solution of acidic acid was found to be 0.0162 S m<sup>-1</sup> at 25°C. Calculate the degree of dissociation of the acid. Molar conductance of acetic acid at infinite dilution is  $390.6 \times 10^{-4}$  Sm<sup>2</sup> mol<sup>-1</sup> at 25°C

- a. 2.6%      b. 9.4%  
 c. 3.7 %      d. 4.7 %

ANSWER KEY	Q.	Ans.								
	1.	a	2.	c	3.	a	4.	c	5.	b
	6.	a	7.	d	8.	b	9.	c	10.	d
	11.	b	12.	c	13.	b	14.	a	15.	c
	16.	b	17.	a	18.	b	19.	c	20.	b
	21.	b	22.	a	23.	b	24.	b	25.	c
	26.	a	27.	b	28.	d	29	a	30.	c
	31.	a	32.	c	33.	c	34.	d		

## Hints and Explanations

1. The two half-reactions can be arranged into an oxidation and reduction half-reaction which when added together from the solubility equilibrium:



$$E = -1.21 \text{ V} - (-0.423 \text{ V})$$

$$= -0.81 \text{ V}$$

$K_{sp}$  is the equilibrium constant and it is related to the standard potential as follow:

$$\log K = \frac{nE^\circ}{0.0592 \text{ V}} = \frac{2(-0.81 \text{ V})}{0.0592 \text{ V}}$$

$$= -27$$

taking the antilog give  $K = 1 \times 10^{-27}$

3. As  $E^\circ_{(\text{Cr}^{3+}/\text{Cr})} = -0.72 \text{ V}$  and  $E^\circ_{(\text{Fe}^{2+}/\text{Fe})} = -0.42 \text{ V}$

$$2\text{Cr} + 3\text{Fe}^{2+} \rightarrow 3\text{Fe} + 2\text{Cr}^{3+}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{6} \log_{10} \frac{(\text{Cr}^{3+})^2}{(\text{Fe}^{2+})^3}$$

$$= (-0.42 + 0.72) - \frac{0.0591}{6} \log_{10} \frac{(0.1)^2}{(0.01)^3}$$

$$= 0.30 - \frac{0.0591}{6} \log_{10} \frac{(0.1)^2}{(0.01)^3}$$

$$= 0.30 - \frac{0.0591}{6} \log_{10} \frac{10^{-2}}{10^{-6}}$$

$$= 0.30 - \frac{0.0591}{6} \log_{10} 10^4$$

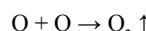
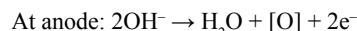
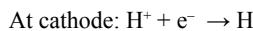
On solving, we get

$$E_{\text{cell}} = 0.2606 \text{ V.}$$

## 6.68 ■ Electrochemistry

4.  $t = 160 \text{ min } 50 \text{ sec} = 9650 \text{ sec}, I = 1 \text{ A}$

volume of  $\text{O}_2$  (released) = ?



According to Faraday's law

$$\text{Volume of gas evolved at NTP} = V = \frac{I t V_e}{96500}$$

Here  $V_e$  = equivalent volume = volume of gas evolved at NTP by 1 Faraday charge.

$$V_e = \frac{22.4}{32} \times 16 = 11.2 \text{ L}$$

$$V = \frac{1 \times 9650 \times 11.2}{96500} = 1.12 \text{ L.}$$

5.  $\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{e}^- ; E_1^\circ = -0.153 \text{ V}$

$$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu} ; E_{\text{II}}^\circ = +0.337 \text{ V}$$

$$\text{Adding Cu}^+ + \text{e}^- \rightarrow \text{Cu} ; E^\circ = ?$$

$$E^\circ = \frac{n_1 E_1 + n_2 E_2}{n} = \frac{1 \times (-0.153) + 2(0.337)}{1}$$

$$= 0.521 \text{ V}$$

6.  $E^\circ = -0.136 \text{ V} - (-0.126 \text{ V})$

$$= -0.010 \text{ V} ; n = 2$$

$$0.22 = -0.010 - \frac{0.0592}{2} \log \frac{[\text{Pb}^{2+}]}{[\text{Sn}^{2+}]}$$

$$= -0.010 - \frac{0.0592}{2} \log \frac{[\text{Pb}^{2+}]}{1.00}$$

$$\log [\text{Pb}^{2+}] = \frac{-0.23(2)}{0.0592} = -7.770$$

$$= -7.8;$$

$$[\text{Pb}^{2+}] = 1.7 \times 10^{-8}$$

$$= 2 \times 10^{-8} \text{ M}$$

7. For  $\text{PbSO}_4(s)$ ,

$$K_{sp} = [\text{Pb}^{2+}][\text{SO}_4^{2-}]$$

$$= (1.0)(1.7 \times 10^{-8})$$

$$= 1.7 \times 10^{-8}$$

8.  $\text{Q} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{QH}_2$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{2} \log_{10} \frac{1}{[\text{H}^+]^2}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - 0.0591 \text{ pH}$$

$$\text{Intercept} = E_{\text{cell}}^\circ = 0.698 \text{ V}$$

$$\text{pH} = 0.698 - \frac{0.491}{0.0591} = 3.5$$

9.  $E^\circ = (0.0592 \text{ V}) \log K/n$

$$= (0.0592 \text{ V}/2) \log (3.76 \times 10^{14})$$

$$= 0.43 \text{ V.}$$

13.  $E^\circ = \frac{0.0592}{n} \text{ V log K};$

$$n = \frac{0.0592 \text{ V}}{E^\circ} \log K$$

$$n = \frac{0.0592 \text{ V}}{0.17 \text{ V}} \log 5.5 \times 10^5;$$

$$n = 2$$

15. Charge passed =  $I \cdot t = 2.5 \times 360 = 900 \text{ C}$

Valency of copper in  $\text{Cu}_2\text{S}$  is 1

So equivalent wt. of copper

$$= \frac{\text{atomic wt.}}{\text{valency}} = \frac{63.5}{1} = 63.5$$

96500 coulomb of charge deposit 63.5 g of copper

therefore 900 C of charge will deposit

$$\frac{63.5}{96500} \times 900 = 0.5 \text{ g of copper}$$

17. Consider the cell,

$$\text{Pt, H}_2(\text{g}) \mid \text{H}^+(1.0 \text{ M}) \parallel \text{H}^+(1 \times 10^{-10} \text{ M}) \mid \text{H}_2, \text{Pt}$$

It is a concentration cell

$$E_{\text{cell}} = 0.0591 \log c_2 / c_1$$

$$= 0.0591 \log 1 \times 10^{-10}$$

$$= -0.591 \text{ V}$$

18.  $Q = I \cdot t = 25 \times 10^{-3} \times 60 = 1.5 \text{ C}$

When 96500 C of charge is passed, the no. of electrons that will flow through the solution =  $6.023 \times 10^{23}$

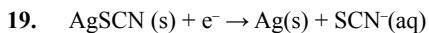
Therefore number of electrons that will flow when 1.5 C of charge is passed

$$= \frac{6.023 \times 10}{96500} \times 1.5 = 9.4 \times 10^{18}$$

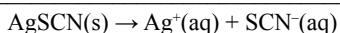
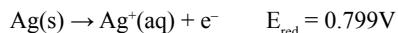
For depositing one calcium atom, number of electrons required = 2

So no. of atoms of calcium required to deposit 9.36  $\times 10^{18}$  electrons is

$$\frac{1}{2} \times (9.4 \times 10^{18}) = 4.7 \times 10^{18}$$



$$E_{\text{red}}^{\circ} = 0.0895 \text{ V}$$



$$E^{\circ} = 0.0895 - 0.799 = -0.710 \text{ V}$$

$$E^{\circ} = \frac{0.0592}{n} \log K_{\text{sp}} = \frac{(-0.710)(1)}{0.0592}$$

$$= -11.993 = -12.0$$

$$K_{\text{sp}} = 10^{-11.993}$$

$$= 1.02 \times 10^{-12}$$

$$= 1 \times 10^{-12}$$

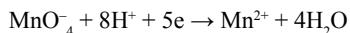
20. According to Nernst equation, the electrode potential of  $\text{Mg}^{2+}/\text{Mg}$  electrode

$$(E) = E^{\circ} + \frac{0.0591}{n} \log [\text{Mg}^{2+}]$$

$$= -2.36 + \frac{0.0591}{2} \log (0.1)$$

$$= -2.36 + 0.02955 (-1) = -2.39 \text{ V}$$

21. The half cell reaction is,



$$E_{\text{MnO}_4^-/\text{Mn}^{2+}} = E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ}$$

$$+ \frac{0.059}{5} \log_{10} \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]}$$

Or

$$E_{\text{RP}} = E_{\text{RP}}^{\circ} + 0.0118 \log_{10} \frac{1 \times 1}{1}$$

$$E_{\text{RP}} = E_{\text{RP}}^{\circ}$$

If  $\text{H}^+ = 10^{-4}$

$$\text{Then } E_{\text{RP}} = E_{\text{RP}}^{\circ} + 0.0118 \log_{10} \frac{1 \times (10^{-4})^8}{1}$$

$$E_{\text{RP}} = E_{\text{RP}}^{\circ} - 0.38 \text{ V}$$

i.e., the couple  $\text{MnO}_4^-/\text{Mn}^{2+}$  shows a decrease in its  $E_{\text{RP}}$  by 0.38 volt or an increase in its  $E_{\text{OP}}$  by 0.38 V and thus less oxidizing power.

22.  $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log K_c$

since  $E_{\text{cell}}$  at equilibrium is 0, therefore 0

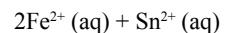
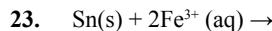
$$= E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log K_c$$

$$E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_c$$

$$0.591 = \frac{0.0591}{1} \log K_c$$

on solving

$$K_c = 1.0 \times 10^{10}$$



$$E_{\text{(cell)}}^{\circ} = E_{\text{(ox)}}^{\circ} + E_{\text{(red)}}^{\circ}$$

$$= E_{\text{Sn/Sn}^{2+}}^{\circ} + E_{\text{(Fe}^{3+}/\text{Fe}^{2+})}^{\circ}$$

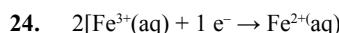
Given

$$E_{\text{Sn}^{2+}/\text{Sn}}^{\circ} = -0.14 \text{ V}$$

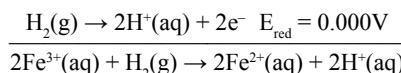
$$E_{\text{Sn}}^{\circ} / \text{Sn}^{2+} = +0.14 \text{ V}$$

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = 0.77 \text{ V}$$

$$E_{\text{cell}}^{\circ} = 0.14 + 0.77 = 0.91 \text{ V}$$



$$E_{\text{red}}^{\circ} = 0.771 \text{ V}$$



$$E^{\circ} = 0.771 - 0.000$$

$$= 0.771 \text{ V}$$

25.  $E = E^{\circ} - \frac{0.0592}{n} \log \frac{[\text{Fe}^{2+}]^2 [\text{H}^+]^2}{[\text{Fe}^{3+}]^2 P_{\text{H}_2}}$

$$[\text{H}^+] = 10^{-\text{pH}} = 1.0 \times 10^{-4}, n = 2$$

$$E = E^{\circ} - \frac{0.0592}{2} \log \frac{(0.010)^2 (1.0 \times 10^{-4})^2}{(0.50)^2 (0.25)}$$

$$= 0.771 - \frac{0.0592}{2} \log (1.6 \times 10^{-11})$$

$$E = 0.771 - \frac{0.0592 (-10.80)}{2}$$

$$= 0.771 + 0.320 = 1.091 \text{ V}$$

26. For the oxidation reaction,  $\text{Tl}^+ \rightarrow \text{Tl}^{3+} + 2e^-$

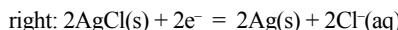
$$E = E^{\circ} - \frac{RT}{nF} \log_{10} \frac{[\text{Oxi.}]}{[\text{Red.}]}$$

## 6.70 ■ Electrochemistry

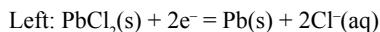
$$= -1.2495 = E^\circ - \frac{0.059}{2} \log_{10} \frac{0.2}{0.02}$$

$$E^\circ = 1.220 \text{ V}$$

27. For the given cell, the Electrode Reduction reaction can be given as

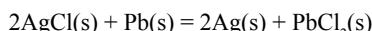


.....(i)



.....(ii)

Subtracting Eq. (ii) from Eq. (i), we get



Now since  $E = a - (1.86 \times 10^{-4} \text{ V K}^{-1})$

(T - 25 K) Therefore

$$\left(\frac{\partial E}{\partial T}\right) = -1.86 \times 10^{-14} \text{ V K}^{-1}$$

Now using the relation

$$\Delta G = -nFE$$

$$= -2(96500 \text{ C mol}^{-1})(0.490 \text{ V})$$

$$= -94570 \text{ C mol}^{-1}$$

$$= -94.57 \text{ K.cal.}$$

28. Relation between  $K_{\text{eq}}$  and  $E_{\text{cell}}$  is

$$E^\circ_{\text{cell}} = \frac{2.303 \text{ RT}}{nF} \log E_{\text{eq}}$$

$$E^\circ_{\text{cell}} = \frac{0.0591}{n} \log E_{\text{eq}}$$

$$0.591 = \frac{0.0591}{1} \log E_{\text{eq}}$$

$$\log E_{\text{eq}} = 10$$

$$E_{\text{eq}} = 1 \times 10^{10}$$

$$29. E_{\text{Cu/Cu}}^{2+} = E^\circ_{\text{Cu/Cu}} - \frac{0.059}{2} \log [\text{Cu}^{2+}]$$

If  $[\text{Cu}^{2+}] = 0$ ,

i.e.,  $[\text{Cu}^{2+}] = 1$

then  $E_{\text{Cu/Cu}}^{2+} = E^\circ_{\text{Cu/Cu}}/2$

or intercept OA =  $E^\circ_{\text{Cu/Cu}}/2 = 0.34$

$$\text{Now } E_{\text{Cu/Cu}}^{2+} = -0.34 - \frac{0.059}{2} \log 0.1 \\ = -0.34 + \frac{0.059}{2}$$

32. (i)  $\text{Cu} = 2\text{Cu}^{2+} + 2\text{e}^-$  ;

$$E^\circ = -0.34 \text{ ;}$$

$$\Delta G^\circ = -2(-0.34)F = 0.68 \text{ F}$$

$$(ii) 2\text{Cu}^{2+} + 2\text{e}^- = 2\text{Cu}^+; E^\circ = +0.15 \text{ ;}$$

$$\Delta G^\circ = -(0.15)F = -0.30 \text{ F}$$

On adding (i) and (ii), we get

$$\text{Cu} + \text{Cu}^{2+} = 2\text{Cu}^+; \Delta G^\circ = +0.38 \text{ F}$$

$$\text{As } -\Delta G^\circ = 2.303 \text{ RT log } K_{\text{eq}}$$

$$\text{So } -0.38 \text{ F} = 2.303 \text{ RT log } K_{\text{eq}}$$

$$-0.38 = 0.0591 \log K_{\text{eq}}$$

$$\log K_{\text{eq}} = -6.429 = 7.571$$

So on taking Antilog we get

$$K_{\text{eq}} = 3.72 \times 10^{-7}$$

33.  $\text{N}^{3+} \rightarrow \text{N}^{5+} + 2\text{e}; E^\circ = -0.94 \text{ V}$

$$2\text{N}^{3+} + 2\text{e} \rightarrow 2\text{N}^{2+} E^\circ = 0.99 \text{ V}$$

$$3\text{N}^{3+} \rightarrow 2\text{N}^{2+} + \text{N}^{5+}$$

$$\text{As } E^\circ_{\text{cell}} = E^\circ_{\text{OP}} + E^\circ_{\text{RP}} \\ \text{HNO}_2/\text{NO}_3^- \quad \text{HNO}_2/\text{NO}$$

$$\text{So } E^\circ_{\text{cell}} = -0.95 + 0.98 = 0.05$$

$$\text{As } E^\circ_{\text{cell}} = \frac{0.059}{2} \log K_c$$

$$\text{So } 0.05 = \frac{0.059}{2} \log K_c$$

On solving  $K_c = 49.53$

34.  $k = 0.0162 \text{ S m}^{-1}; c = 0.01 \text{ mol dm}^{-3}$   
 $= 10 \text{ mol m}^{-3}$

$$\Lambda m = \frac{k}{c} = \frac{0.0162 \text{ S m}^{-1}}{10 \text{ mol m}^{-3}}$$

$$= 16.2 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

$$\Lambda^\circ m = 390.6 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1} \text{ (given)}$$

$$\alpha = \frac{\Lambda m}{\Lambda^\circ m} = \frac{16.2 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}}{390.6 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}}$$

$$= 0.047 = 4.7\%$$

# CHAPTER 7

# Chemical Kinetics

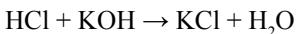
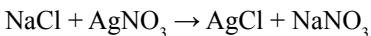
## Chapter Contents

Rates of chemical reactions; Order of reactions; Rate constant; First order reactions; Temperature dependence of rate constant (Arrhenius equation) and Various levels of multiple-choice questions.

## CHEMICAL KINETICS

Chemical kinetics ('kinesis' meaning movement) is the study of rate and mechanism of a reaction and factors effecting it like temperature, pressure catalyst, radiations etc.

- On the basis of rate, reactions are characterized as slow, moderate and very fast types.
- Very fast reactions take  $10^{-14}$ – $10^{-16}$  s for their completion and they are not studied under kinetics, these are studied by flash photolysis and spectrographic methods. example, – Ionic reactions



- Very slow reactions like rusting of iron or blackening of white lead, formation of water at room temperature and burning of coal are also not studied under kinetics.
- Moderate reactions like molecular reactions (most of the organic reactions) are studied under

kinetics example, (i) Hydrolysis of sugar or ester  
(ii) Decomposition of  $\text{N}_2\text{O}_5$ ,  $\text{H}_2\text{O}_2$ ,  $\text{NH}_4\text{NO}_2$  etc.

## Rate of Reaction

It is defined as “The rate of change of concentration of a reactant or a product per unit time” that is it is nothing but it is the per unit mole of rate of decomposition of any reactant or formation of product.

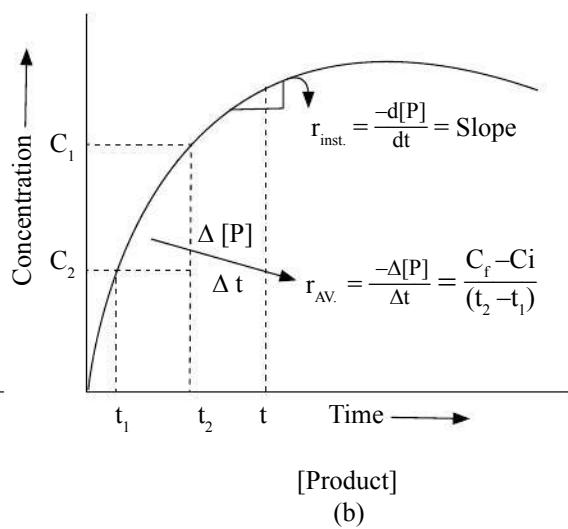
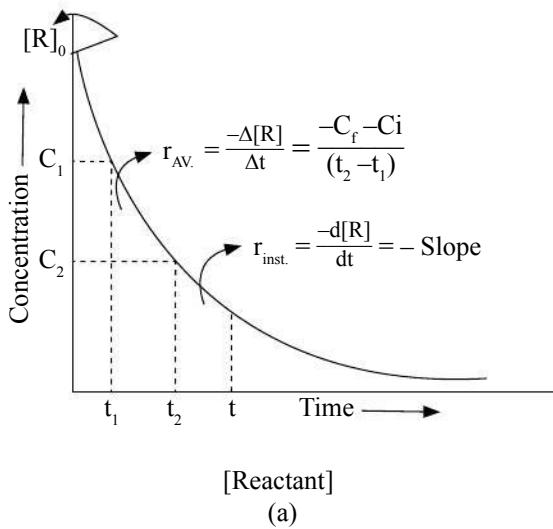
$$\text{Rate of reaction (r)} = \frac{\text{C}_1 - \text{C}_2}{\text{t}_2 - \text{t}_1}$$

As rate of reaction varies greatly with time, so generally, average reaction rate and instantaneous reaction rates are used. Average rate ways to is the rate at some particular instant of time and is equal to the time rate of change of the active mass of any of the reactants or any of the products.

example For a reaction  $\text{A} \rightarrow \text{P}$

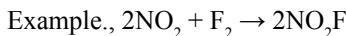
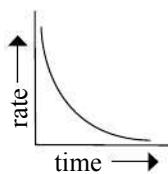
$$\text{Rate of disappearance of A} = -\frac{\Delta[\text{A}]}{\Delta T}$$

$$\text{Rate of appearance of P} = -\frac{\Delta[\text{P}]}{\Delta T}$$

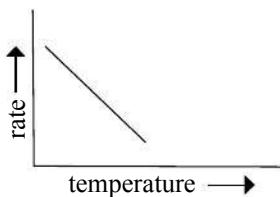


## Features of Rate of Reaction

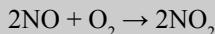
- It is always a positive quantity.
- It is proportional to the active masses of the reactant.
- It is measured by measuring active mass or molar concentration of a reactant or a product as a function of time.
- Rate of reaction for reactants decreases with time as concentration of reactant decreases.



Here rate of reaction is measured by decrease in concentration of F<sub>2</sub>.



### REMEMBER



The only reaction with negative temperature coefficient.

## Units of Rate of Reaction

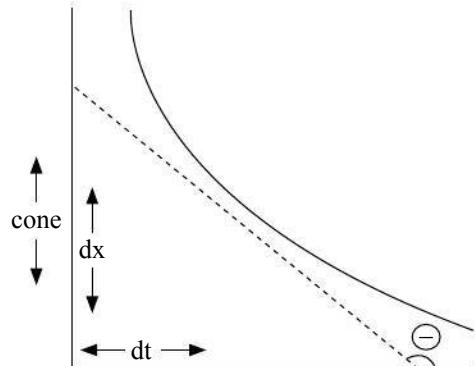
$\text{mol L}^{-1} \text{ time}^{-1}$  or  $\text{atm time}^{-1}$ . (gaseous substance).

## Instantaneous Rate of Reaction

As average reaction rate fails to predict rate at a particular moment of time so we use instantaneous rate which is equal to small change in concentration (dx) during a small interval of time (dt). It is given as  $dx/dt$ .

$$R_{\text{instant}} = \frac{dc}{\Delta t}$$

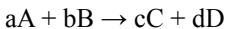
$\Delta t \rightarrow 0$   
limit



Instantaneous Reaction Rate

- $dx/dt = \tan \theta = \text{slope of curve}$
- It can be written for any of the reactant or the product in terms of stoichiometric coefficients (V<sub>j</sub>) which is negative for reactants and positive for products as follows:

$$\frac{dx}{dt} = \frac{1}{V_j} \frac{d(J)}{dt}$$



$$\text{Rate w.r.t. } [A] = -\frac{d[A]}{dt} \times \frac{1}{a}$$

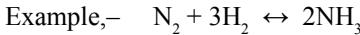
$$\text{Rate w.r.t. } [B] = -\frac{d[B]}{dt} \times \frac{1}{b}$$

$$\text{Rate w.r.t. } [C] = -\frac{d[C]}{dt} \times \frac{1}{c}$$

$$\text{Rate w.r.t. } [D] = -\frac{d[D]}{dt} \times \frac{1}{d}$$

- For the reactants, negative sign indicates decrease of concentration and for products positive sign indicates increase in concentration.
- For a reversible reaction at dynamic equilibrium, net reaction rate is always zero as

$$(dx/dt)_r = (dx/dt)_B$$



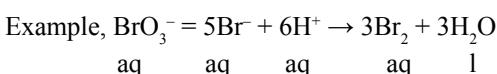
$$\text{For } N_2: \frac{dx}{dt} = \frac{-dN_2}{dt}$$

$$\text{for } H_2: \frac{-dx}{dt} = \frac{-dH_2}{dt}$$

$$\text{for } NH_3: \frac{dx}{dt} = \frac{dNH_3}{dt}$$



$$\frac{dH_2O_2}{dt} = \frac{-1}{2} \frac{dH^+}{dt} = \frac{-1}{3} \frac{dI^-}{dt} = \frac{dI_3^-}{dt} = \frac{1}{2} \frac{dH_2O}{dt}$$



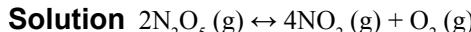
$$\frac{-dBrO_3^-}{dt} = \frac{-1}{5} \frac{dBr^-}{dt} = \frac{-1}{6} \frac{dH^+}{dt} = \frac{1}{3} \frac{dBr_2}{dt} = \frac{1}{3} \frac{dH_2O}{dt}$$

## Illustrations

- Write the expression for the rate of following gaseous reaction:



which takes place in a closed vessel. If the concentration of  $NO_2$  increases by  $1.6 \times 10^{-4}$  mol litre $^{-1}$  in 4 second, find the rate of reaction and rate of change of concentration of  $N_2O_5$ .



Rate of reaction ( $r$ )

$$= -\frac{1}{2} \frac{d[N_2O_5]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

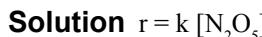
$$\text{Rate of reaction} = \frac{1}{4} \times \frac{1.6 \times 10^{-4}}{4}$$

$$= 1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{Change in conc. of } N_2O_5 = \frac{1}{2} \times \frac{1.6 \times 10^{-3}}{4}$$

$$= 2.0 \times 10^{-3}$$

- When  $[N_2O_5] = 0.22$  M, the rate of decomposition of  $N_2O_5$  is  $1.3 \times 10^{-4}$  mol  $L^{-1} s^{-1}$ . What is the value of  $k$  for this first order reaction?

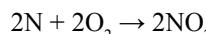


$$k = \frac{r}{[N_2O_5]}$$

$$= \frac{1.3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}}{0.22 \text{ M}}$$

$$= 5.91 \times 10^{-4} \text{ s}^{-1}$$

- Show by using rate law, how much rate of the reaction



will change if the volume of the reaction vessel is reduced to one-third of its value.



When volume is reduced to one-third, the concentration of each reactant increases by three times.

$$r_2 = k [3NO]^2 [3O_2] \quad \dots \dots \text{ (ii)}$$

On dividing equation (ii) by equation (i), we get,

$$\frac{r_2}{r_1} = \frac{k [3NO]^2 [3O_2]}{k [NO]^2 [O_2]} = 27$$

$$r_2 = 27 r_1$$

So the reaction is increased by 27 times.

- The reaction,  $2N_2O_5 \rightarrow 4NO_2 + O_2$ , is forming  $NO_2$  at the rate of 0.0076 mole/lit/sec at some time:
  - What is the rate of change of  $[O_2]$  at this time?

## 7.4 ■ Chemical Kinetics

- (b) What is the rate of change of  $[N_2O_5]$  at this time?  
 (c) What is the rate of reaction at this time?

**Solution** Rate =  $-\frac{1}{2} \frac{d[N_2O_5]}{dt} = +\frac{1}{4} \frac{d[NO_2]}{dt}$   
 $= +\frac{d[O_2]}{dt}$

Here  $\frac{d[NO_2]}{dt} = 0.0076$  mole/lit/sec

- (a) Rate of appearance of  $O_2$   
 $= \frac{1}{4} \times$  rate of appearance of  $NO_2$   
 $\frac{d[O_2]}{dt} = \frac{1}{4} \times \frac{d[NO_2]}{dt}$   
 $= \frac{1}{4} \times 0.0076$   
 $= 0.0019$  mole/lit/sec
- (b) Rate of disappearance of  $N_2O_5$   
 $= \frac{1}{2} \times$  rate of appearance of  $NO_2$   
 $= -\frac{d[N_2O_5]}{dt} = \frac{1}{2} \times \frac{d[NO_2]}{dt}$   
 $\frac{d[N_2O_5]}{dt} = -\frac{1}{2} \times 0.0076$   
 $= -0.0038$  mole/lit/sec
- (c) Rate of reaction =  $\frac{1}{4} \times \frac{d[NO_2]}{dt}$   
 $= \frac{1}{4} \times 0.0076 = 0.0019$  mol/lit/sec

5. The reaction  $2A + B + C \rightarrow D + E$  is found to be of first order in A. Second order in B and zero order in C.

- (i) Give the rate law for the reaction in the form of differential equation.  
 (ii) What is the effect in rate of increasing concentration of A, B and C two times?

**Solution** (i) The rate law for the reaction is given by

$$\frac{dx}{dt} = k [A] [B]^2 [C]^0$$

$$\frac{dx}{dt} = k [A] [B]^2$$

- (ii) On increasing the concentration of A, B and C two times then,

$$\frac{dx}{dt} = k [2A] [2B]^2 [2C]^0$$

$$\frac{dx}{dt} = k [2A] [2B]^2$$

$$= 8 k [A] [B]^2$$

Therefore, rate increases by 8 times

6. Dinitro pentoxide decomposes as follows:



Given

$$\frac{d[N_2O_5]}{dt} = k_1 [N_2O_5]$$

$$\frac{d[NO_2]}{dt} = k_2 [N_2O_5]$$

$$\frac{d[O_2]}{dt} = k_3 [N_2O_5]$$

What is the relation between  $k_1$ ,  $k_2$  and  $k_3$ ?

**Solution**  $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2} O_2(g)$

Rate w.r.t.  $N_2O_5$  or  $NO_2$  or  $O_2$  may be expressed as follows in the form of relation

$$-\frac{d[N_2O_5]}{dt} = +\frac{1}{2} \frac{d[NO_2]}{dt} = +2 \frac{d[O_2]}{dt}$$

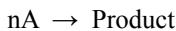
On substituting the given values in the question

$$k_1 [N_2O_5] = k_2/2 [N_2O_5] = 2k_3 [N_2O_5]$$

$$2k_1 = k_2 = 4k_3$$

### Reaction Rate or Velocity Constant

To explain it, let us consider this reaction:



$$-\frac{dx}{dt} \propto [A]^n$$

$$\text{or } -\frac{dx}{dt} = K[A]^n$$

According to Rate Law equation,

If  $[A]^n = 1$  than

$$-\frac{dx}{dt} = K \quad (\text{At a particular temperature})$$

K = Rate constant or specific reaction rate

Hence at unity concentration rate of a reaction is equal to rate constant.

- **K Temperature** (that is rate constant increases with increase of temperature)
- Rate constant also depends upon presence of catalyst and nature of reactant.
- Rate constant does not depend upon concentration pressure and volume.
- Unit of rate constant is  $(\text{mole/litre})^{1-n} \text{ time}^{-1}$  or  $\text{litre}^{n-1} \text{ mol}^{1-n} \text{ time}^{-1}$  (Here n = order of reaction).

## Factors Effecting Rate of Reaction and Rate Constant

### Physical State of Reactants

Rate also changes with physical state.

$$\begin{array}{c} \text{Gaseous state} > \text{liquid states} > \text{solid states} \\ \xrightarrow{\quad \text{Decreasing order of rate of reaction} \quad} \end{array}$$

### Temperature

Rate of reaction increases with the increase of temperature as it increases the number of effective collisions. It is observed that for every  $10^\circ\text{C}$  rise in temperature  $-dx/dt$  or rates becomes double to triple as the number of molecules with energy greater than activation energy becomes two – three times.

$$\text{Temp. Coefficient } (\mu) = \frac{K \text{ at } t^\circ\text{C} + 10^\circ\text{C}}{K \text{ at } t^\circ\text{C}}$$

The value of temperature coefficient lies in between 2–3.

In case we increase temperature by more than  $10^\circ\text{C}$  the above relation can be given as:

$$\frac{K_{T_2}}{K_{T_1}} = (\mu)^{\Delta T/10}$$

[Here  $\Delta T = T_2 - T_1$ ]

$$\log_{10} \frac{K_{T_2}}{K_{T_1}} = \frac{\Delta T}{10} \log_{10} \mu$$

$$\frac{K_{T_2}}{K_{T_1}} = \text{Antilog} \left[ \frac{\Delta T}{10} \log_{10} \mu \right]$$

### Concentration

Rate increases with the increase of concentration as due to more number of reactants there are more collisions.

Rate of reaction ( $dx/dt$ )  $\propto$  Concentration

### Pressure

For gaseous reactants rate varies with pressure just like concentration.

$$\frac{dx}{dt} \propto \text{Pressure} \quad (\text{as } P \propto C)$$

### Surface Area

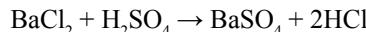
Greater the surface area, faster is the rate of reaction due to more number of active sites.

Rate ( $dx/dt$ )  $\propto$  Surface area

### Nature of Reactant and Product

- For ionic reactants reaction rate is fast as activation energy is zero for them.

example,



- Molecules have slow reaction rate due to need of more activation energy. Example,



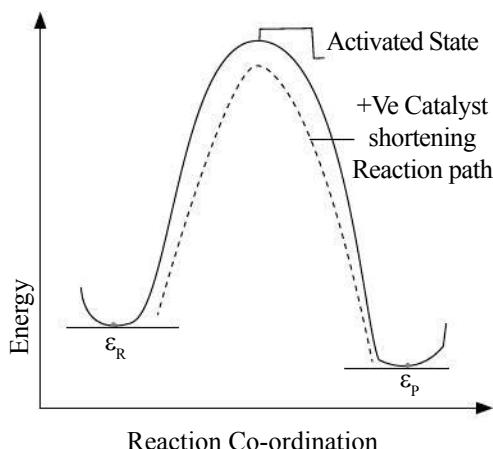
### Radiation

Rate of photochemical reactions depends upon intensity of light radiations.

$$\frac{dx}{dt} \propto \text{Intensity of radiation}$$

### Positive Catalyst

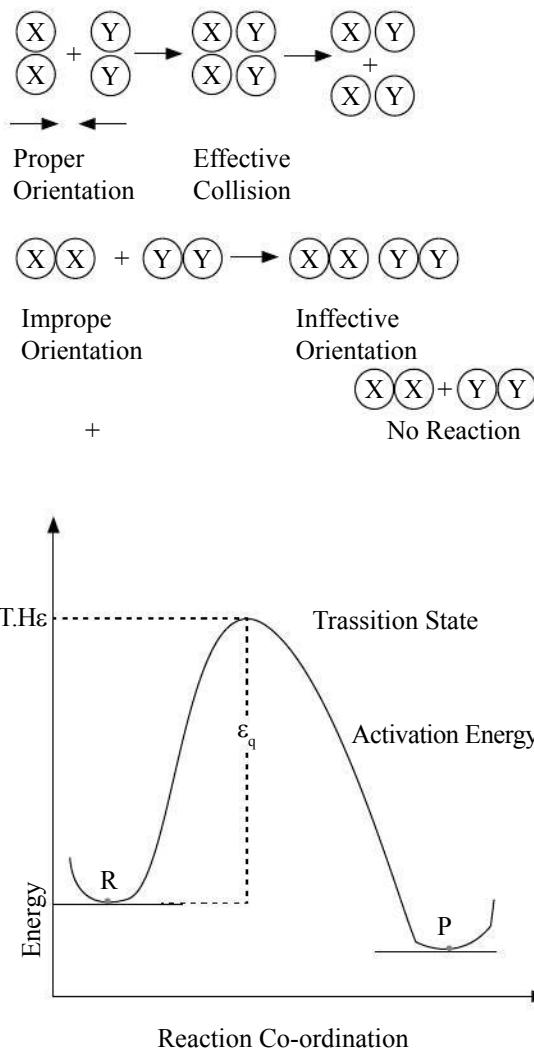
It increases the rate of a reaction by decreasing the activation energy by accepting a new alternative smaller path for the reaction. It is reverse in case of negative catalyst to that of positive catalyst. Catalysts are more effective in ‘Solid powdered form’ due to larger surface area, that is, more active sites.



## COLLISION THEORY

A reaction takes place as the reacting molecules undergo collisions with one another that is a chemical reaction is the result of effective collisions.

For effective collisions: (a) Colliding molecules must have sufficient potential energy. (b) Collision should be with proper orientation.



The minimum energy needed to convert a reactant into product is called Threshold energy. (T.H.E)

or

It is the minimum amount of energy possessed by reacting molecules in order to have effective collisions for the formation of product.

Threshold energy = Potential energy of reactant + Ea

- Rate of reaction according to this theory is given as  
Rate = f. P. Z

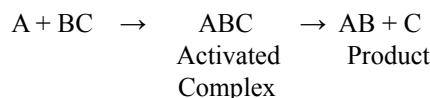
Here f is fraction of molecules with potential energy greater than threshold energy or collision crossing over the energy barrier having energy  $\approx$  or  $>$  Ea.

$$f = e^{-E_a/RT}$$

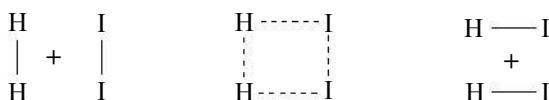
P is the orientation factor.

Z is the collision frequency which is proportional to  $U_{r.m.s}$  and temperature dependent.

- Transition state or activated state theory or absolute rate theory was developed by Henry Eyring.



example.,



## ACTIVATION ENERGY

It is the minimum amount of additional external energy needed to convert a reactant into product or to make potential energy of the reactant equals to threshold energy. It is denoted by Ea.

Ea = Threshold energy – Potential energy of reactants

Or

Average kinetic energy of reactants

$$\text{Rate of Reaction} \propto \frac{1}{\text{Ea}}$$

Hence lower the activation energy faster is the rate of the reaction.

## Determination of Activation Energy

- Larger the value of Ea of a reaction, smaller is k.
- Larger the value of Ea of a reaction, greater will be the influence of change in temperature on rate constant.

## Arrehenius Equation

It is used to evaluate energy of activation and to show the effect of temperature on rate constant as follows

$$K = Ae^{-E_a/RT}$$

Or

$$\log_{10} K = \log_{10} A - \frac{E_a}{2.303 RT} \quad \dots \dots \dots (1)$$

- Here A is frequency or Arrhenius or pre exponential factor or maximum rate constant of the reaction. It signifies total number of collisions or frequency of binary collisions per unit volume per unit time.
- When Ea is zero or temperature is infinite

$$K = Ae^0 = A$$

Here  $e^{-E_a/RT}$  is known as Boltzmann factor showing fraction of molecules with  $E > E_a$ .

- At two different temperatures  $T_1$  and  $T_2$

$$E_a = \frac{2.303 R T_1 T_2}{T_2 - T_1} \log_{10} \frac{K_2}{K_1}$$

$$\log_{10} \frac{K_2}{K_1} = \frac{E_a}{2.303 R} \frac{(T_2 - T_1)}{(T_1 T_2)}$$

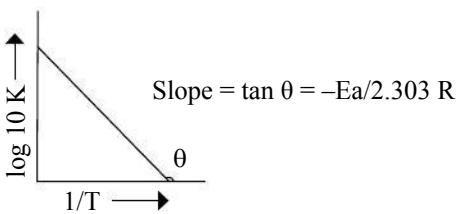
Here  $K_1$  and  $K_2$  are constant at temperature  $T_1$  and  $T_2$  K respectively.

### Graph between $\log_{10} K$ and $1/T$

When a graph is plotted between  $\log K$  and  $1/T$  a straight line with a negative slope is obtained. Here slope is equal to  $-E_a / 2.303R$  that is  $E_a = -2.303 R \times \text{slope}$  as

$$\log_{10} K = \log_{10} A - \frac{E_a}{2.303 R} \left[ \frac{1}{T} \right]$$

$$Y = C + MX$$



$$\Delta H = H_p - H_R$$

$$\Delta H = (Ea)_f - (Ea)_b$$

$$E_{TH} = H_R + (Ea)_f$$

or

$$E_{TH} = H_p + (Ea)_b$$

### In Exothermic Reactions

$\Delta H$  is negative.

As potential energy of reactant > potential energy of product

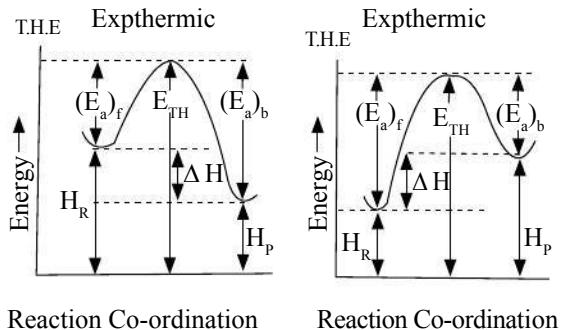
$E_a$  of backward reaction >  $E_a$  of forward reaction

### In Endothermic Reactions

$\Delta H$  is positive.

As potential energy of reactant < potential energy of product

$E_a$  of backward reaction <  $E_a$  of forward reaction



### REMEMBER

#### ■ Modified Arrhenius Equation:

$$\frac{d \ln K}{dt} = \frac{E}{RT^2}$$

### Illustrations

7. Find the activation energy of a reaction whose rate constant is tripled by a  $10^\circ\text{C}$  rise in temperature, in the activity of  $27^\circ\text{C}$ .

**Solution**  $K_2/K_1 = 3$ ,

$$T_1 = 273 + 37 = 310 \text{ K}$$

$$\log_{10} \frac{K_2}{K_1} = \frac{E_a}{2.303 R} \frac{(T_2 - T_1)}{(T_1 T_2)}$$

$$\log_{10} 3 = \frac{E_a}{2.303 \times 8.314} \frac{(310 - 300)}{(300 \times 310)}$$

$$E_a = 84.97 \text{ kJ mol}^{-1}$$

8. For first order gaseous reaction  $\log k$  when plotted against  $1/T$  it give a straight line with a slope of  $-8000$ . Calculate the activation energy of the reaction.



Here p, q are experimental quantities which may or may not be equal to the respective stoichiometric coefficients (x, y).

## Order of Reaction

Order of reaction is defined as number of reactants which determine rate of reaction.

Or

Number of reactants whose molar concentration changes during the chemical reaction.

Or

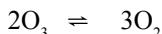
It is the sum of exponents raised on active masses of reactants in a rate law equation.

- It is an experimental value.
- It may be zero, negative or in fraction.
- It determines rate of reaction.
- Order of reaction depends upon temperature, pressure and concentration etc.
- Anything in excess is not counted in order of reaction. Example, In hydrolysis of ester and sugar water is in excess so it is neglected for order.
- Order of reaction is determined by the slowest step of the reaction.
- High order reactions are rare due to less chance of effective collisions between molecules.
- For an elementary reaction order of reaction must be equal to molecularity of the reaction

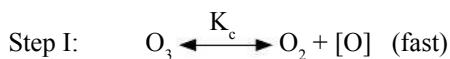
### REMEMBER

Rate constant and order for various reacting species is an experimental finding and cannot be predicted directly from the stoichiometry of the balanced reaction.

Example,



### Mechanism



$$\text{Rate} = K [\text{O}_3] [\text{O}] \quad \dots\dots\dots(1)$$

$$K_c = \frac{[\text{O}_2] [\text{O}]}{[\text{O}_3]} \quad \text{or} \quad [\text{O}] = K_c \cdot \frac{[\text{O}_3]}{[\text{O}_2]} \quad \dots\dots(2)$$

Hence

$$\text{Rate} = K [\text{O}_3] \cdot K_c \cdot \frac{[\text{O}_3]}{[\text{O}_2]} = K' [\text{O}_3]^2 [\text{O}_2]^{-1}$$

Order = 1

## First Order Reaction

Here the reaction rate is determined by one concentration variable term only.



$$-\frac{dx}{dt} \propto [a]^1$$

$$dx/dt = K [a]$$

At after time 't' the concentration is  $(a - x)$  so

$$\frac{dx}{dt} \propto (a - x)$$

$$\frac{dx}{dt} = K (a - x)$$

On integrating

$$-\ln(a - x) = Kt + c$$

$$\text{When } t = 0, x = 0$$

$$c = -\ln a$$

$$-\ln(a - x) = Kt - \ln a$$

$$Kt = \ln a - \ln(a - x) = \ln \frac{a}{(a - x)}$$

$$K = \frac{2.303}{t} \log_{10} \frac{a}{(a - x)}$$

or

$$t = \frac{2.303}{K} \log_{10} \frac{N_0}{N}$$

$$\text{Hence } N = N_0 e^{-KT}$$

$$\text{or } A = A_0 \cdot e^{-KT}$$

This is known as Wilhelmy's equation which shows decrease in concentration with respect to time.

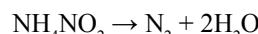
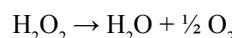
Here t = time period

K = rate constant

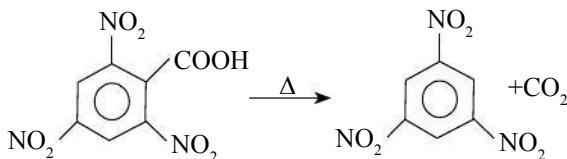
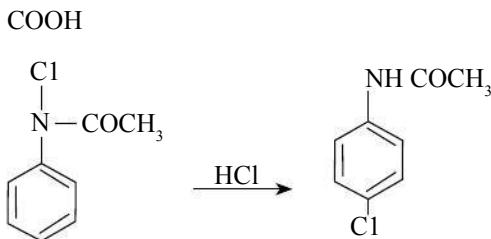
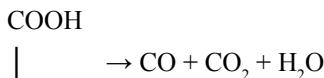
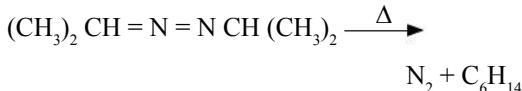
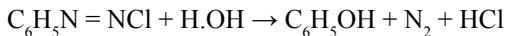
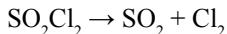
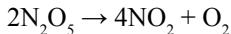
$A_0$  or  $N_0$  = initial amount or activity

A or N = amount or activity after 't' time.

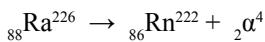
### Examples of First Order Reaction:



## 7.10 ■ Chemical Kinetics



All radioactive decays are first order example.,



### Features of First Order Reactions

- Unit of K is  $\text{time}^{-1}$ .
- K does not depend upon concentration unit Or change in concentration.
- $t_{1/2}$  does not depend upon initial concentration (a). It depends only upon rate constant.

If  $t = t_{1/2}$  or  $t_{50}$

$$X = a/2$$

$$\text{Then } t_{50} \text{ or } t_{1/2} = \frac{2.303}{K} \log_{10} \frac{a}{a-a/2}$$

$$t_{1/2} = \frac{2.303}{K} \log_{10} 2 = \frac{2.303}{K} \times 0.3010$$

$$t_{1/2} = \frac{0.693}{K}$$

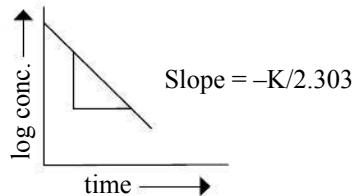
- If  $t_{75}$  or  $\frac{3}{4}a$  a value of 'X' is used

$$t_{75} = 2 \times t_{50}$$

- If  $t_{87.5}$  is used

$$t_{87.5} = 3 \times t_{50}$$

- If a graph is plotted between time 't' and  $\log_{10}$  (a or conc.), a straight line is obtained whose slope is equal to  $\frac{-K}{2.303}$ .



- Time taken for the completion of any fraction of reaction does not depend upon the initial concentration of the reactant and for 'n' fraction it is given as

$$t_{1/n} = \frac{2.303}{K} \log_{10} \frac{n}{n-1}$$

### Pseudo-Unimolecular Reaction

Those reactions which are not truly of the first order but under certain conditions become reactions of the first order.

- Here molecularity is more than one but order of reaction is always first.

Example (1) Hydrolysis of ethyl acetate

$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$			
Initially	a	0	0
After 't' time	(a-x)	x	x
At $\infty$	0	a	a

For it rate constant K is given as

$$k = \frac{2.303}{t} \log_{10} \frac{V_0 - V_\infty}{V_t - V_\infty}$$

$$\text{As } a = V_0 - V_\infty \text{ and } (a-x) = (V_t - V_\infty)$$

Here  $V_\infty$  = volume at infinite

$V_0$  = initial volume

$V_t$  = volume at t time

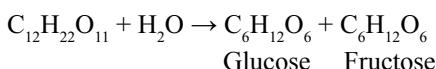
**Case I:** When  $V_0$  is not given

$$K = \frac{2.303}{t} \log_{10} \frac{V_\infty}{V_\infty - V_t}$$

**Case II:** When  $V_\infty$  is not given

$$K = \frac{2.303}{t} \log_{10} \frac{V_0}{V_t}$$

Example, (2) Hydrolysis of sugar



For it rate constant is given as

$$t = \frac{2.303}{K} \log_{10} \frac{r_\infty - r_t}{r_\infty}$$

Here  $r_0$  = initial optical rotation

$r_\infty$  = rotation at infinite dilution.

$r_t$  = rotation at t time.

## Illustrations

11. A first order reaction completes 50 per cent in 69.3 minute. How much time it will take for 90 per cent completion?

**Solution**  $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.3} = 0.01$

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$0.01 = \frac{2.303}{t} \log_{10} \frac{100}{10}$$

$$t = \frac{2.303}{0.01} = 230.3 \text{ minute.}$$

12. A reaction obeying second order in A is 50 per cent complete after 450 minute. If  $[A]_0 = 1.35 \text{ M}$ . Calculate the value of rate constant.

**Solution**  $t = 450 \text{ minute}$

$$a = 1.35 \text{ M}$$

$$x = 0.675 \text{ M}$$

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

$$k = \frac{1}{450} \times \frac{0.675}{1.35(0.675)}$$

$$= 1.646 \times 10^{-3} \text{ mol}^{-1} \text{ litre min}^{-1}$$

13. A substance, A decomposes by a first order reaction. Starting initially with  $[A] = 2.00 \text{ M}$ , after 200 min  $[A] = 0.250 \text{ M}$ . Calculate for this reaction (i)  $t_{1/2}$  and (ii) k.

**Solution** First order reaction,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$= \frac{2.303}{200} \log_{10} \frac{2.00}{0.25}$$

$$= \frac{2.303}{200} \log_{10} 8$$

$$= 0.0104 \text{ min}^{-1}$$

For first order reaction,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0104}$$

$$= 66.63 \text{ min}$$

14. Thermal decomposition of a compound is of first order. If 50 per cent of a sample of the compound is decomposed in 120 minutes, how long will it take for 90 per cent of the compound to decompose?

**Solution**  $k = \frac{0.693}{t_{50\%}} = \frac{0.693}{120 \text{ min}}$

$$t = \frac{2.303}{k} \log_{10} \frac{a}{a-x}$$

$$t_{90\%} = \frac{2.303}{0.693 \setminus 120 \text{ min}} \log_{10} \frac{100}{100-90}$$

$$= \frac{2.303 \times 120 \text{ min}}{0.693} \log_{10} 10$$

$$= \frac{2.303 \times 120 \text{ min}}{0.693} \times 1 = 399 \text{ min}$$

15. Show that in case of a first order reaction, the time required for 99.9 per cent of the reaction to take place is ten times that required for half of the reaction.

**Solution**  $t = \frac{2.303}{k} \log_{10} \frac{[A]_a}{[A]_t}$

$$= \frac{2.303}{k} \log_{10} \frac{a}{a-x}$$

$$= \frac{2.303}{k} \log_{10} \frac{1}{1-f}$$

Here f is the fraction of reaction completed in time, t.

$$t_{50\%} = \frac{2.303}{k} \log_{10} \frac{1}{1-0.5} = \frac{2.303}{k} \log_{10} 2 \dots (i)$$

$$t_{99.9\%} = \frac{2.303}{k} \log_{10} \frac{1}{1-0.999}$$

$$= \frac{2.303}{k} \log_{10} \frac{1}{0.001}$$

$$= \frac{2.303}{k} \log_{10} \frac{1}{10^{-3}} = \frac{2.303}{k} \log_{10} 10^3 \dots (ii)$$

## 7.12 ■ Chemical Kinetics

On dividing equation (ii) by (i), we get

$$\begin{aligned} \frac{t_{99.9\%}}{t_{50\%}} &= \frac{2.303}{k} \times \frac{k}{2.303} \times \log \frac{10^3}{\log 2} \\ &= \frac{3.000}{0.3010} = 9.967 = 10 \end{aligned}$$

- 16.** What will be the initial rate of a reaction if its rate constant is  $10^{-3}$  min $^{-1}$  and the concentration of reactant is 0.2 mol dm $^{-3}$ ? How much of the reactant will be converted into products in 200 minutes?

**Solution** As K has unit min $^{-1}$  so given reaction is of first order.

$$\text{Rate} = k [ ]^1$$

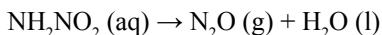
$$\text{Rate} = 10^{-3} \times [0.2]^1 = 2 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$$

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$10^{-3} = \frac{2.303}{200} \log_{10} \frac{100}{(100-x)}$$

$$x = 18.12\% \text{ D.t.}$$

- 17.** The half time of first order decomposition of nitramide is 2.1 hour at 15°C.



If 6.2 g of  $\text{NH}_2\text{NO}_2$  is allowed to decompose, calculate:

- (a) time taken for  $\text{NH}_2\text{NO}_2$  is decompose 99 per cent  
 (b) Volume of dry  $\text{N}_2\text{O}$  produced at this point measured at STP.

**Solution**  $t = \frac{2.303}{k} \log_{10} \frac{a}{a-x}$

$$\text{If } t = t/2, x = a/2$$

$$t_{1/2} = \frac{2.303}{k} \log_{10} \frac{a}{a-a/2} \quad \dots \dots \text{(i)}$$

$$\text{If } t = t_{99\%}, x = 99a/100$$

$$t_{99\%} = \frac{2.303}{k} \log_{10} \frac{a}{a-99a/100} \dots \dots \text{(ii)}$$

From equation (i) and (ii)

$$t_{99\%} = \frac{\log_{10} 100}{\log_{10} 2} \times t_{1/2}$$

$$= \frac{2}{0.3010} \times 2.1 = 13.95 \text{ hour}$$

Mole of  $\text{N}_2\text{O}$  formed

$$\begin{aligned} &= \frac{99}{100} \times \text{mole of } \text{NH}_2\text{NO}_2 \text{ taken} \\ &= \frac{99}{100} \times \frac{6.2}{62} = 0.099 \end{aligned}$$

$$\begin{aligned} \text{Thus, volume of } \text{N}_2\text{O} \text{ formed at STP} \\ &= 0.099 \times 22.4 \\ &= 2.217 \text{ litre} \end{aligned}$$

- 18.** A substance reacts according to first order kinetics and rate constant for the reaction is  $1 \times 10^{-2}$  sec $^{-1}$ . If its initial concentration is 1 M.

- (a) What is initial rate?  
 (b) What is rate after 1 minute?

**Solution** (a) Initial rate =  $k [ ]^1 = 1 \times 10^{-2} \times [1]$   
 $= 1 \times 10^{-2}$

$$\text{Rate} = 1 \times 10^{-2} \text{ mol litre}^{-1} \text{ sec}^{-1}$$

$$(b) k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$10^{-2} = \frac{2.303}{1 \times 60} \log_{10} \frac{1}{(1-x)}$$

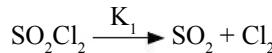
$$(1-x) = 0.549$$

$$\text{Rate after 1 minute} = k [ ] \text{ after 1 minute}$$

$$= k [0.549] = 10^{-2} [0.549]$$

$$\text{Rate after 1 minute} = 5.49 \times 10^{-3} \text{ mol litre}^{-1} \text{ sec}^{-1}$$

- 19.** The reaction



is a first order reaction with  $k_1 = 2.2 \times 10^{-5}$  sec $^{-1}$  at 302°C. What percentage of  $\text{SO}_2\text{Cl}_2$  will get decomposed in 90 minutes when the reaction is carried out at 302°C?

**Solution**  $k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$

$$\text{Here } k = 2.2 \times 10^{-5} \text{ sec}^{-1}$$

$$t = 90 \text{ minutes} = 90 \times 60 = 5400 \text{ sec}$$

$$\text{So } 2.2 \times 10^{-5} = \frac{2.303}{5400} \log_{10} \frac{a}{a-x}$$

$$\log_{10} \frac{a}{a-x} = 0.0516$$

$$\frac{a}{a-x} = \text{antilog}(0.0516) = 1.127$$

$$a = 1.127 a - 1.127 x$$

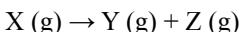
$$0.127 a = 1.127 x$$

$$\frac{x}{a} = \frac{0.127}{1.127} = 0.113$$

$$= 11.3\%$$

### Concentration replaced by other quantities in first order reactions

#### Reaction involving gases in a closed vessel or container



**Case I:** If the initial pressure of X (g) be  $P_0$  and after time 't', suppose its pressure be P,

$$\text{then } P_0 \propto a$$

$$P \propto (a-x)$$

$$K = \frac{2.303}{t} \log_{10} \frac{P_0}{P}$$

**Case II:** If the initial pressure of X (g) be  $P_0$  and after time 't' the total pressure of the reaction mixture is  $P_t$ , then

$$P_0 \propto a$$

$$(a-x) \propto 2P_0 - P_t$$

$$K = \frac{2.303}{t} \log_{10} \frac{P_0}{2P_0 - P_t}$$

**Case III:** If the total pressure at any time 't' is given to be  $P_t$  and total pressure after a long period of time is  $P'$ .

$$P_t \propto (a+x)$$

$$P' \propto 2a$$

$$\text{Also } P' - P_t \propto (a-x)$$

$$K = \frac{2.303}{T} \log_{10} \frac{P'}{2(P' - P_t)}$$

**Case IV:** If the total pressure of product at any time 't' is given to be  $P_t$  and total pressure of product after a long period is  $P'$ .

$$P_0 = \frac{P'}{2}$$

$$P_0 - x = \frac{1}{2}(P' - P_t)$$

$$K = \frac{2.303}{T} \log_{10} \frac{P'}{P' - P_t}$$

■ For the decomposition of  $N_2O_5$  and  $NH_4NO_2$  and hydrolysis of benzene diazonium chloride the relation used is given as

$$K = \frac{2.303}{t} \log_{10} \frac{V_\infty}{V_\infty - V_t}$$

■ For the decomposition of  $H_2O_2$  the relation used is given as

$$K = \frac{2.303}{t} \log_{10} \frac{V_0}{V_t}$$

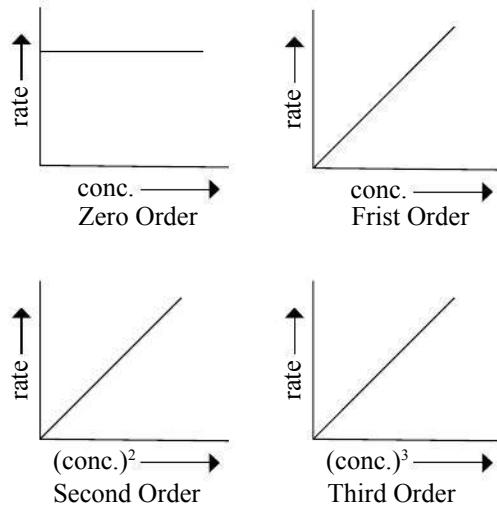
### Methods for Determining Order of Reaction

Order of a reaction is determined mainly by:

(i) **Graphical methods:** Here graphs are plotted between rate and concentration to find the order of the reaction.

$$[\text{Rate} = k(\text{concentration})^n]$$

#### Plots of Rate vs Concentration



(ii) **Van't Hoff differential method**

$$\text{As } \frac{dx}{dt} \propto C^n$$

$$\text{So } \frac{-dC_1}{dt} = KC_1^n \quad \dots(1)$$

$$\frac{-dC_2}{dt} = KC_2^n \quad \dots(2)$$

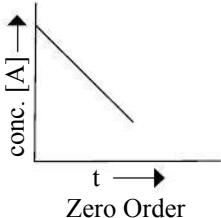
On taking log and subtracting both equation number (1) and (2), we get

$$\frac{n = \log(-dC_1/dt) - \log(-dC_2/dt)}{\log C_1 - \log C_2}$$

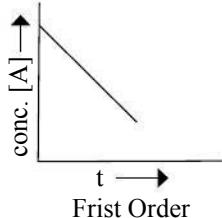
## 7.14 ■ Chemical Kinetics

Note: The values of  $-dC_1/dt$  and  $-dC_2/dt$  can be observed from 'C' vs 't' plots.

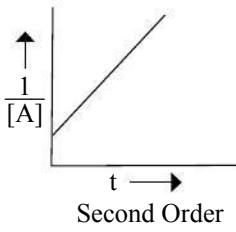
**Plots from integrated rate equations:** When the graphs are plotted between  $1/(a-x)^{n-1}$  and time t a straight line will be formed which decides order of reaction as follows:



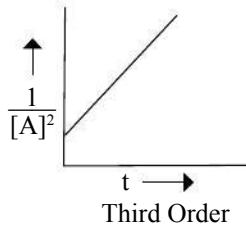
Zero Order



Frist Order



Second Order



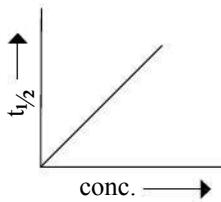
Third Order

$$\log_{10} \frac{(t_{1/2})_1}{(t_{1/2})_2} = (n - 1) \log_{10} \left( \frac{a_2}{a_1} \right)$$

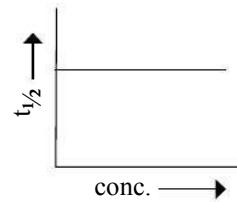
Hence

$$n = 1 + \frac{\log(t_{1/2})_1 - \log(t_{1/2})_2}{\log a_2 - \log a_1}$$

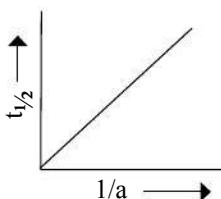
Here n is the order of reaction.



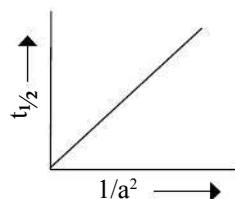
Zero Order



Frist Order



Second Order



Third Order

(iii) **Half life method:** It is used when the rate law involves only one concentration term.

$$t_{1/2} \propto (a)^{1-n}$$

or

$$t_{1/2} \propto 1/a^{n-1}$$

For two different concentrations

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left( \frac{a_2}{a_1} \right)^{n-1}$$

On taking logarithms on both sides

(iv) **Hit and Trial Method (Integration method):** Here we put the values of a, x, t in kinetic equation of various orders and the equation that gives the most constant values of rate constant K for a series of time intervals gives the order of the reaction.

(v) **Initial concentration method:** Here first measure the initial rate of the reaction, that is the rate at the beginning of the reaction so that the known concentration of the different reactants have not changed noticeably.

Reaction	Order	Rate law Equation	Expression	Unit of K
$A \rightarrow P$	Zero	Rate = $K [A]^0$ Rate = $K$	$K = \frac{1}{t} [A_o - A]$	Mol lit <sup>-1</sup> time <sup>-1</sup>
$A \rightarrow P$	First	Rate = $K [A]^1$	$K = \frac{2.303}{t} \log_{10} \frac{[A_o]}{[A]}$	Time <sup>-1</sup>
$2A \rightarrow P$	Second	Rate = $K[A]^2$	$K = \frac{1}{t} \left( \frac{1}{A} - \frac{1}{A_o} \right)$	Lit mol <sup>-1</sup> tome <sup>-1</sup>
$A + B \rightarrow P$	Second	Rate = $K [A] [B]$	$K = \frac{2.303}{t (a-b)} \log \frac{b[A]}{a[B]}$	Lit <sup>2</sup> mol <sup>-2</sup> time <sup>-1</sup>
$3A \rightarrow P$	Third	Rate = $K[A]^3$	$K = \frac{1}{2t} \left( \frac{1}{(A)^2} - \frac{1}{(A_o)^2} \right)$	Mol <sup>-2</sup> time <sup>-1</sup>

Now change the initial concentration of only one of the reactants keeping the initial concentration of all the reactants same as before and determine the initial rate again. This data achieved gives the order with respect to this reactant. Now for another reactants repeat this process.

## Illustrations

### 20. Rate of a reaction

$A + B \rightarrow C$  is given below as a function of differential concentrations of A and B.

Exp.	[A]	[B]	Rate
	Mol lit <sup>-1</sup>	Mol lit <sup>-1</sup>	Mol lit <sup>-1</sup> time <sup>-1</sup>
1	0.01	0.01	0.005
2	0.02	0.01	0.010
3	0.01	0.02	0.005

Determine order of reaction with respect to A and B and also calculate the half life of A in the reaction?

**Solution** Rate =  $k [A]^x [B]^y$

$$0.005 = k [0.01]^x [0.01]^y \quad \dots \dots \dots (1)$$

$$0.010 = k [0.02]^x [0.01]^y \quad \dots \dots \dots (2)$$

$$0.005 = k [0.01]^x [0.02]^y \quad \dots \dots \dots (3)$$

For x

Divide eq. (2) by (1)

$$(2) = (2)^x$$

$$x = 1$$

For y :

Divide eq. (3) by (1)

$$Y = 0$$

$$\text{Rate} = k [A]^1 [B]^0$$

$$0.005 = k [0.01]^1 [0.01]^0$$

$$k = \frac{0.005}{0.01} = 0.5$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.5} = 1.386 \text{ time}$$

21. The data given below are for the reaction of NO and  $\text{Cl}_2$  to form  $\text{NOCl}$  at 295 K.

[ $\text{Cl}_2$ ]	[NO]	Initial rate ( $\text{mol litre}^{-1} \text{ sec}^{-1}$ )
0.05	0.05	$1 \times 10^{-3}$
0.15	0.05	$3 \times 10^{-3}$
0.05	0.15	$9 \times 10^{-3}$

- (a) What is the order w.r.t NO and  $\text{Cl}_2$  in the reaction?  
 (b) Write the rate expression.  
 (c) Calculate the rate constant.  
 (d) Determine the reaction rate when concentration of  $\text{Cl}_2$  and NO are 0.2 M and 0.4 M respectively.

**Solution**  $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$

$$\text{Rate} = k [\text{Cl}_2]^m [\text{NO}]^n \quad \dots \dots \dots (i)$$

Here m and n are order of reaction w.r.t  $\text{Cl}_2$  and NO respectively.

According to given data:

$$1 \times 10^{-3} = k [0.05]^m [0.05]^n \quad \dots \dots \dots (ii)$$

$$3 \times 10^{-3} = k [0.15]^m [0.05]^n \quad \dots \dots \dots (iii)$$

$$9 \times 10^{-3} = k [0.05]^m [0.15]^n \quad \dots \dots \dots (iv)$$

From equation (ii) and (iii),

$$m = 1$$

From equation (ii) and (iv),

$$n = 2$$

(a) Order w.r.t NO is 2 and w.r.t  $\text{Cl}_2$  is 1

(b) Rate expression (r) =  $k [\text{Cl}_2]^1 [\text{NO}]^2$

$$(c) \text{Rate constant (k)} = \frac{r}{[\text{Cl}_2]^1 [\text{NO}]^2}$$

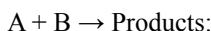
$$= \frac{1 \times 10^{-3}}{[0.05]^1 [0.05]^2} = 8 \text{ litre}^2 \text{ mol}^{-2} \text{ sec}^{-1}$$

$$(d) r = k [\text{Cl}_2]^1 [\text{NO}]^2$$

$$= 8 [0.2]^1 [0.4]^2$$

$$= 0.256 \text{ mol litre}^{-1} \text{ sec}^{-1}$$

22. The following data are for the reaction



[A]	[B]	Initial rate (mol litre <sup>-1</sup> sec <sup>-1</sup> )
0.1	0.1	$4.0 \times 10^{-4}$
0.2	0.2	$1.6 \times 10^{-3}$
0.5	0.1	$1.0 \times 10^{-2}$
0.5	0.5	$1.0 \times 10^{-2}$

- (a) What is the order with respect to A and B for the reaction?
- (b) Calculate the rate constant.
- (c) Determine the reaction rate when the concentrations of A and B are 0.2 M and 0.35 M, respectively.

### Solution

According to rate law equation

$$R = k [A]^m [B]^n$$

Rate law for four cases is as follows:

$$4.0 \times 10^{-4} = k (0.1)^m (0.1)^n \quad \dots \dots \text{(i)}$$

$$1.6 \times 10^{-3} = k (0.2)^m (0.2)^n \quad \dots \dots \text{(ii)}$$

$$1.0 \times 10^{-2} = k (0.5)^m (0.1)^n \quad \dots \dots \text{(iii)}$$

$$1.0 \times 10^{-2} = k (0.5)^m (0.5)^n \quad \dots \dots \text{(iv)}$$

- (a) On dividing equation (iii) by (i), we get

$$\frac{1.0 \times 10^{-2}}{1.0 \times 10^{-4}} = \frac{k (0.5)^m (0.1)^n}{k (0.1)^m (0.1)^n}$$

$$1 = (1/5)^n$$

$$n = 0$$

So the order of reaction with respect to B is zero.

On dividing equation (i) by (iii), we get

$$\frac{4.0 \times 10^{-4}}{1.0 \times 10^{-2}} = \frac{k (0.1)^m (0.1)^n}{k (0.5)^m (0.1)^n}$$

$$4 \times 10^{-2} = (1/5)^m$$

$$(0.2)^m = 0.04$$

$$(0.2)^m = (0.2)^2$$

$$m = 2$$

So the order of reaction with respect to A is two.

- (b) On substituting the values of m and n in equation (ii), we get

$$1.6 \times 10^{-3} \text{ mol lit}^{-1} \text{ sec}^{-1} = k (0.2 \text{ M})^2 (0.2 \text{ M})^0$$

$$1.6 \times 10^{-3} \text{ mol lit}^{-1} \text{ sec}^{-1} = 0.04 \text{ M}^2 k$$

$$k = \frac{1.6 \times 10^{-3} \text{ mol lit}^{-1} \text{ sec}^{-1}}{0.04 \text{ M}^2}$$

$$= 4.0 \times 10^{-2} \text{ mol}^{-1} \text{ lit sec}^{-1}$$

$$(c) R = k[A]^2 [B]^0$$

$$R = 4 \times 10^{-2} \times (0.2)^2 (0.35)^0$$

$$= 4 \times 10^{-2} \times 0.04 = 1.6 \times 10^{-3} \text{ mol lit}^{-1} \text{ sec}^{-1}$$

### Enhance Your Knowledge

#### Elementary and Complex Reactions

It is interesting to know that a balanced chemical equation never shows us a true picture of how the reaction is taking place as very rarely a reaction gets completed in one step only.

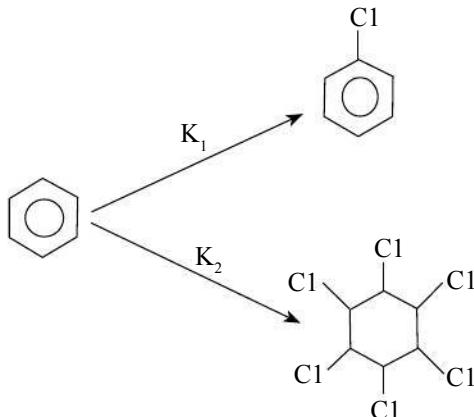
- The reaction which occurs in one step only is known as an elementary reaction and when a sequence of such reactions (mechanism) provides us the desired products these reactions are known as complex reactions.
- Such reactions may be consecutive, reverse and side reactions.

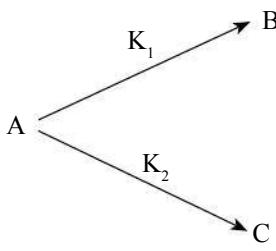
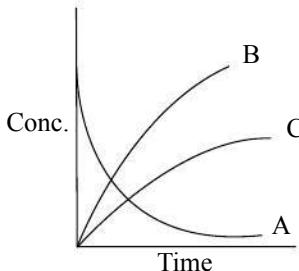
Example, In the complete combustion of an alkane the final products are always CO<sub>2</sub>, and water, however during this reaction a series of many elementary reactions take place during which alcohol, aldehyde and acid are formed.

- **Rate law equation for reactions involving parallel and side reactions.**

**Parallel Reactions:** In such a reaction, the reactant decomposes or reacts in more than one ways.

Example,





$$R_1 = K_1 [A] = \frac{d[B]}{dt}$$

$$R_2 = K_2 [A] = \frac{d[C]}{dt}$$

$$R_1 + R_2 = \frac{-d[A]}{dt} = (K_1 + K_2) [A]$$

If  $K_{\text{Av.}} = K_1 + K_2$  and  $R_{\text{Av.}} = R_1 + R_2$

Then  $R_v = K_{\text{Av.}} [A]$

Ratio of concentration of B and C can be calculated as follows:

$$\frac{[B]}{[C]} = \frac{K_1}{K_2}$$

Rate constant of parallel reaction can be find out as follows:

$$K = K_1 + K_2 = \frac{2.303}{T} \log_{10} \frac{[A_0]}{[A]}$$

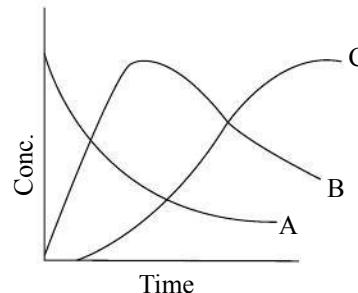
Here  $A_0$  = Initial concentration of A

$A$  = Amount of A left after time  $t$

Fraction yield of B and C can be find out as follows:

- Fraction yield of B =  $K_1/(K_1 + K_2)$  or  $K_{\text{av.}}$
- Fraction yield of C =  $K_2/(K_1 + K_2)$  or  $K_{\text{av.}}$

### Consecutive or Successive reaction



Here rate of disappearance of A =  $K_1 + K_2 [A]$

$$[A]_t = [A]_0 e^{-K_1 t}$$

$$[B]_t = \frac{K_1 [A]_0}{K_2 - K_1} [e^{-K_1 t} - e^{-K_2 t}]$$

Time at which [B] becomes maximum can be find out by using the relation

$$t_{\text{max.}} = \frac{2.303}{(K_2 - K_1)} \log_{10} \frac{K_2}{K_1}$$

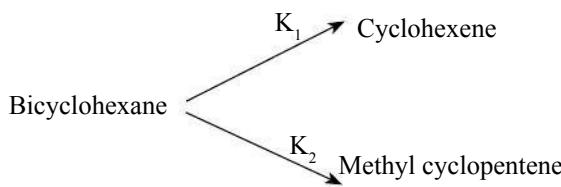
$$[B]_{\text{max.}} = \frac{K_1}{K_2 - K_1} [A_0] (K_2/K_1)^{K_2/K_1 - K_2} - (K_2/K_1)^{[K_2/K_1 - K_2]}$$

Or

$$[B]_{\text{max.}} = \frac{[A_0]}{(K_2 - K_1)} [K_2 (1 - e^{-K_1 t}) - K_1 (1 - e^{-K_2 t})]$$

### Illustrations

23. Bicyclohexane was found to undergo two parallel first order rearrangements. At 730 K, the first order rate constant for the formation of cyclohexane was measured as  $1.28 \times 10^{-4} \text{ s}^{-1}$ , and for the formation of methyl cyclopentene the rate constant was  $3.6 \times 10^{-5} \text{ s}^{-1}$ . What is the percentage distribution of the rearrangement products?

**Solution**


$$\text{Percentage of cyclohexene} = \frac{k_1}{k_1 + k_2} \times 100$$

$$= \frac{1.28 \times 10^{-4}}{1.28 \times 10^{-4} + 3.6 \times 10^{-5}} \times 100$$

$$= \frac{1.28}{1.64} \times 100$$

$$= 78 \text{ percent}$$

Hence percentage of methylcyclopentene = 22 per cent.

**Reversible or opposing reaction**

	P	$K_1$	Q
Initially	a	$K_2$	0
After 't' time	$(a - x)$		x
Conc. at eq.	$(a - x_c)$		$x_c$

On putting and solving, we get

$$(K_1 + K_2) = \frac{2.303}{t} \log_{10} \frac{X_c}{X_c - X}.$$

**Zero Order Reaction**

In such reactions rate of reaction is independent of concentration of the reactants.

$$\frac{-dx}{dt} \propto [\text{concentration}]^0$$

that is,  $dx/dt = K$

On integration we get

$$x = Kt + C$$

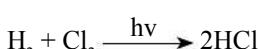
If  $t = 0, c = 0$  then

$$x = Kt$$

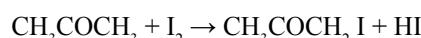
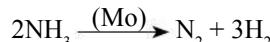
$$K = x/t$$

- Unit of K is  $\text{mol L}^{-1} \text{ time}^{-1}$

Example,— Photochemical reactions



(Studied over water surface)


**Features of Zero Order Reaction:**

- The concentration of the reactant decreases linearly with time.

$$[\text{A}]_t = [\text{A}]_0 - kt$$

- Rate = K (at all concentrations)

- $t^{1/2} \propto a$  (initial concentration)

**Photo Chemical Reactions**

Those reactions which take place only in the presence of light are called photochemical reactions. Example, Photosynthesis and formation of HCl

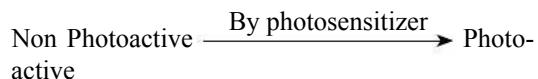
- For such reactions  $\Delta G^\circ$  (standard Gibb's free energy change) can be positive also.

Example, In the synthesis of carbohydrate and HCl formation.

- Red light has lowest energy. Photochemical reactions which can be initiated by red light can be initiated

- Such reactions are not effected by temperature however effected by intensity of light radiations.

**Photosensitizer:** It is a substance which when added to a reaction mixture helps to start the photochemical reaction but itself does not undergo any chemical change. Example, Chlorophyll in photosynthesis and Hg vapours in dissociation of  $\text{H}_2$ .



**Luminiscence:** It is the Emission of cold light without action of heat.

**Chemiluminiscence:** It is the conversion of chemical energy in to cold light energy.

Example, In glow worm, the glow is due to oxidation of luciferin protein. (Bioluminescence).

**Flourescence:** Here emission of light stops when radiation is cut off at once that is glow is as long as radiation occurs Example, CaF<sub>2</sub>

**Phosphorescence:** Here emission of light occurs for some time even after light radiation is cut off. Example, ZnS

### Rhuantum efficiency:

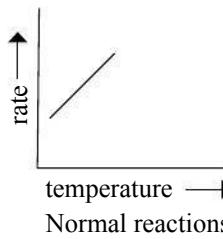
$\Phi$  = Number of molecules reacting in a

$$\frac{\text{given time}}{\text{no. of quanta absorbed at the same time}}$$

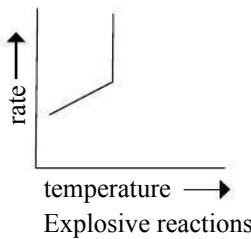
Example,

- for HCl  $\Phi$  is high (As both steps are exothermic) but for HBr  $\Phi$  is low (as second step is endothermic).
- **Vision:** Here retina undergoes geometrical isomerisation by absorbing a photon of light.

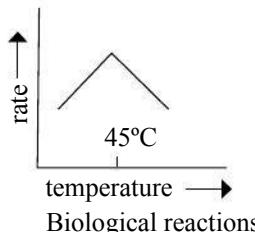
## VARIOUS PLOTS



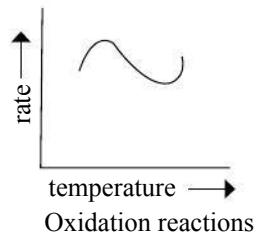
Normal reactions



Explosive reactions



Biological reactions



Oxidation reactions

## Solved Problems from the IITs

1. In the Arrhenius equation for a certain reaction, the values of A and Ea (energy of activation) are  $4 \times 10^{13} \text{ sec}^{-1}$  and  $98.6 \text{ kJ mol}^{-1}$  respectively. If the reaction is of first order, at what temperature will its half life period be 10 minute?

[IIT 1990]

**Solution** According to Arrhenius equation,

$$k = A e^{-E_a/R T}$$

$$\log_e k = \log_e A - \frac{E_a}{RT}.$$

$$2.303 \log_{10} K = 2.303 \log_{10} A - \frac{E_a}{RT}.$$

For a first order reaction

$$t_{1/2} = \frac{0.693}{k}$$

$$\text{So } k = \frac{0.693}{600} \text{ sec}^{-1}$$

$$(t_{1/2} = 10 \text{ min} = 600 \text{ sec})$$

$$= 1.1 \times 10^{-3} \text{ sec}^{-1}$$

$$\log (1.1 \times 10^{-3}) = \log (4 \times 10^{13})$$

$$-\frac{98.6 \times 10^3}{2.303 \times 8.314 \times T}$$

$$T = 310.95 \text{ K}$$

[IIT 1991]

**Solution**  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$

As on decomposition of 2 moles of N<sub>2</sub>O<sub>5</sub>, 4 moles of NO<sub>2</sub> and 1 mole of O<sub>2</sub> are produced so total pressure after completion corresponds to 5 moles and initial pressure of 2 moles.

Initial pressure of N<sub>2</sub>O<sub>5</sub>,

$$P_0 = \frac{2}{5} \times 584.5 = 233.8 \text{ mm Hg}$$

After 30 minutes,

the total pressure = 284.5 mm Hg



$$P_0 - 2P \quad 4P \quad P$$

$$P_0 + 3P = 284.5$$

## 7.20 ■ Chemical Kinetics

$$3P = 284.5 - 233.8 = 50.7 \text{ mm Hg}$$

$$P = \frac{50.7}{3} = 16.9 \text{ mm Hg}$$

Pressure of  $\text{N}_2\text{O}_5$  after 30 minutes

$$= 233.8 - (2 \times 16.9)$$

$$= 200 \text{ mm Hg}$$

$$k = \frac{2.303}{30} \log_{10} \frac{233.8}{200}$$

$$= 5.2 \times 10^{-3} \text{ min}^{-1}$$

3. The gas phase decomposition of dimethyl ether follows first order kinetics



The reaction is carried out in a constant volume container at  $500^\circ\text{C}$  and has a half life of 14.5 minutes. Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure after 12 minutes? Assume ideal gas behaviour.

[IIT 1993]

**Solution**  $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.5} = 0.047793 \text{ min}^{-1}$

Let the pressure of dimethyl ether 12 minutes be 'P' atm.

According to first order equation

$$k = \frac{2.303}{t} \log_{10} \frac{P_0}{P}$$

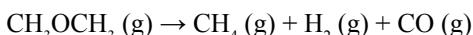
$$\log_{10} \frac{0.4}{P} = \frac{0.047793 \times 12}{2.303} = 0.2490$$

$$\frac{0.4}{P} = 1.7743$$

$$P = \frac{0.4}{1.7743} = 0.2254 \text{ atm}$$

Decrease in pressure

$$X = 0.4 - 0.2254 = 0.1746 \text{ atm}$$



$$P_0 - X \quad X \quad X \quad X$$

$$\text{Total pressure} = P_0 + 2X$$

$$= 0.4 + 2 \times 0.1746$$

$$= 0.7492 \text{ atm}$$

4. From the following data from the reaction between A and B.

[A] mol L <sup>-1</sup>	[B] mol L <sup>-1</sup>	Initial rate mol litre <sup>-1</sup> sec <sup>-1</sup> 300K	320K
$2.5 \times 10^{-4}$	$3.0 \times 10^{-5}$	$5.0 \times 10^{-4}$	$2.0 \times 10^{-3}$
$5.0 \times 10^{-4}$	$6.0 \times 10^{-5}$	$4.0 \times 10^{-3}$	—
$1.0 \times 10^{-3}$	$6.0 \times 10^{-5}$	$1.6 \times 10^{-2}$	—

Calculate

- (i) The order of reaction with respect to A and B.
- (ii) The rate constant at 300 K.
- (iii) The energy of activation.
- (iv) The pre-exponential factor.

[IIT 1994]

**Solution** Rate =  $k [A]^x [B]^y$

From experiment (1)

$$5.0 \times 10^{-4} = k [2.5 \times 10^{-4}]^x [3.0 \times 10^{-5}]^y \quad \dots(i)$$

From experiment (2)

$$4.0 \times 10^{-3} = k [5.0 \times 10^{-4}]^x [6.0 \times 10^{-5}]^y \quad \dots(ii)$$

Dividing equation (ii) by (i), we get

$$\frac{4.0 \times 10^{-3}}{5.0 \times 10^{-4}} = 2^x \cdot 2^y = 8$$

From experiment (3)

$$1.6 \times 10^{-2} = k [1.0 \times 10^{-3}]^x [6.0 \times 10^{-5}]^y \quad \dots(iii)$$

Dividing equation (iii) by (ii), we get

$$\frac{1.6 \times 10^{-2}}{4.0 \times 10^{-3}} = 2^x = 4$$

$$x = 2 \text{ and } y = 1$$

Thus order with respect to A is second and order with respect to B is first.

(ii) Rate =  $k [A]^2 [B]$

From experiment (1)

$$5 \times 10^{-4} = k [2.5 \times 10^{-4}]^2 [3.0 \times 10^{-5}]$$

$$k = \frac{5 \times 10^{-4}}{[2.5 \times 10^{-4}]^2 [3.0 \times 10^{-5}]}$$

$$= 2.67 \times 10^8 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

(iii) According to Arrhenius equation

$$\log_{10} \frac{2.0 \times 10^{-3}}{5.0 \times 10^{-4}} = \frac{Ea}{2.303 \times 8.314} \times \frac{20}{300 \times 320}$$

$$Ea = \frac{2.303 \times 8.314 \times 300 \times 320}{20} \times \log_{10} 4$$

$$= 55.333 \text{ kJ mol}^{-1}$$

$$(iv) \log_{10} k = \log_{10} A - \frac{Ea}{2.303 RT}$$

$$\log_{10} \frac{A}{k} = \frac{55.333}{2.303 \times 8.314 \times 300} = 9.633$$

$$\frac{A}{k} = 4.29 \times 10^9$$

$$A = 4.29 \times 10^9 \times 2.67 \times 10^8$$

$$= 1.145 \times 10^{18}$$

5. At 380°C, the half life period for the first order decomposition of H<sub>2</sub>O<sub>2</sub> is 360 minute. The energy of activation of the reaction is 200 kJ mole<sup>-1</sup>. Calculate the time required for 75 per cent decomposition at 450°C.

[IIT 1995]

$$K_1 \text{ at } 653 \text{ K} = \frac{0.693}{t_{1/2}} = \frac{0.693}{360}$$

$$= 1.925 \times 10^{-3} \text{ min}^{-1}$$

$$\log_{10} \frac{K_2}{K_1} = \frac{Ea}{2.303 R} \frac{(T_2 - T_1)}{(T_1 T_2)}$$

$$\log \frac{K_2}{1.925 \times 10^{-3}}$$

$$= \frac{200 \times 10^3}{2.303 \times 8.314} \frac{[723 - 653]}{[653 \times 723]}$$

$$K_2 = 0.068 \text{ min}^{-1}$$

$$t = \frac{2.303}{K_2} \log_{10} \frac{a}{a - x}$$

$$= \frac{2.303}{0.068} \log_{10} \frac{100}{25} = 20.39 \text{ minute}$$

6. The time required for 10 per cent completion of a first order reaction at 298 K is equal to that required for its 25 per cent completion at 308 K. If the pre-exponential factor for the reaction is  $3.56 \times 10^9 \text{ sec}^{-1}$ , calculate its rate constant at 318 K and also the energy of activation.

[IIT 1997]

**Solution**  $k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$

At 298 K

$$x = 10, a = 100$$

$$k_{298} = \frac{2.303}{t_1} \log_{10} \frac{100}{90} \quad \dots \text{(i)}$$

At 308 K,

$$a = 100, x = 25, (a-x) = 75$$

$$k_{308} = \frac{2.303}{t_2} \log_{10} \frac{100}{75} \quad \dots \text{(ii)}$$

On dividing equation (ii) by (i)

$$t_1 = t_2$$

$$\text{so } \frac{k_{308}}{k_{298}} = 2.73$$

$$\log_{10} \frac{k_{308}}{k_{298}} = \frac{E}{2.303 R} (1/T_1 - 1/T_2)$$

$$\log_{10} 2.73 = \frac{E}{2.303 \times 8.314} \left( \frac{1}{308} - \frac{1}{298} \right)$$

$$E = 76.622 \text{ kJ mol}^{-1}$$

Similarly we can solve for  $k_{318}$  which is equal to  $9.22 \times 10^{-4} \text{ s}^{-1}$

7. The rate constant of a reaction is  $1.5 \times 10^7 \text{ s}^{-1}$  at 50°C and  $4.5 \times 10^7 \text{ s}^{-1}$  at 100°C. Calculate the Arrhenius parameter A and Ea.

[IIT 1998]

**Solution**  $\log_{10} \frac{k_2}{k_1} = \frac{Ea}{2.303 R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$

$$\log_{10} \frac{4.5 \times 10^7}{1.5 \times 10^7}$$

$$= \frac{Ea}{2.303 \times 8.314} \left( \frac{1}{323} - \frac{1}{373} \right)$$

$$Ea = 2.2 \times 10^4 \text{ J mol}^{-1}$$

$$\log_{10} k = \log_{10} A - \frac{Ea}{2.303 RT}$$

$$\log_{10} (1.5 \times 10^7)$$

$$= \log_{10} A - \frac{2.2 \times 10^4}{2.303 \times 8.314 \times 323}$$

$$A = 5.42 \times 10^{10} \text{ s}^{-1}$$

8. The rate constant for an isomerisation reaction,  $A \rightarrow B$  is  $4.5 \times 10^{-3} \text{ min}^{-1}$ . If the initial concentration of A is 1 M, calculate the rate of reaction after one hour.

[IIT 1999]

**Solution** The dimension of the rate constant of the reaction ( $\text{min}^{-1}$ ) indicates that it is first order reaction.

$$K = \frac{2.303}{t} \log_{10} \frac{1}{1-x}$$

$$4.5 \times 10^{-3} = \frac{2.303}{1 \times 60} \log_{10} \frac{1}{1-x}$$

On solving, we get

$$x = 0.237$$

After one hour

$$[B] = 0.237 \text{ M}$$

$$\text{So } [A] = 1 - 0.237 = 0.763 \text{ M}$$

Rate after 1 hour =  $K [A]^n$

$$= 4.5 \times 10^{-3} \times 0.763$$

$$= 3.43 \times 10^{-3} \text{ M/min}$$

9. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol<sup>-1</sup>.

[IIT 2000]

**Solution** According to Arrhenius equation

$$K = Ae^{-E_a/R T}$$

Let  $k_{500}$  and  $k_{400}$  be the rate constants at temperatures 500 K and 400 K (in presence of catalyst) respectively.  $E_{500}$  and  $E_{400}$  be the activation energies at temperatures 500 K and 400 K respectively.

$$K_{500} = Ae^{-E_{500}/R \times 500} \quad \dots \text{(i)}$$

$$K_{400} = Ae^{-E_{400}/R \times 400} \quad \dots \text{(ii)}$$

Given  $k_{500} = k_{400}$  (same rates in presence and absence of a catalyst)

On comparing equation (i) with (ii)

$$\frac{E_{500}}{R \times 500} = \frac{E_{400}}{R \times 400}$$

$$\text{or } \frac{E_{500}}{5} = \frac{E_{400}}{4}$$

$$E_{500} = \frac{E_{400}}{4} \times 5 \quad \dots \text{(iii)}$$

$$\text{given } E_{500} = E_{400} + 20$$

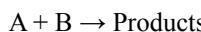
On substituting the values in equation (iii)

$$E_{400} + 20 = E_{400} \times 1.25$$

$$E_{400} = \frac{20}{0.25} = 80 \text{ kJ mol}^{-1}$$

$$\text{so } E_{500} = 80 + 20 = 100 \text{ kJ mol}^{-1}$$

10. For the given reaction,



following data were obtained:

	[A] <sub>0</sub>	[B] <sub>0</sub>	R <sub>0</sub> mol lit <sup>-1</sup> sec <sup>-1</sup>
1.	0.1M	0.2M	0.05
2.	0.2M	0.2M	0.10
3.	0.1M	0.1M	0.05

(i) Write the rate law expression.

(ii) Find the rate constant.

[IIT 2004]

**Solution** Let order with respect to A and B are  $\alpha$  and  $\beta$  respectively. Rate law expression may be given as

$$\text{Rate} = k [A]^\alpha [B]^\beta$$

$$0.05 = k [0.1]^\alpha [0.2]^\beta \quad \dots \text{(i)}$$

$$0.10 = k [0.2]^\alpha [0.2]^\beta \quad \dots \text{(ii)}$$

$$0.05 = k [0.1]^\alpha [0.1]^\beta \quad \dots \text{(iii)}$$

On dividing equation (i) by (ii), we obtain

$$1/2 = [1/2]^\alpha$$

that is,  $\alpha = 1$

On dividing equation (i) by (iii), we obtain

$$1 = [2]^\beta$$

that is,  $\beta = 0$

$$\text{Rate} = k [A]^1 [B]^0$$

On putting the value of  $\alpha$  and  $\beta$  in eq. (i)

$$0.05 = k [0.1]^1 [0.2]^0$$

$$k = 0.5 \text{ sec}^{-1}$$

11. A constant temperature and volume X decomposes as,



$P_x$  is the partial pressure of X.

Observation No.	Time (min)	$P_x$ (in mm Hg)
1	0	800
2	100	400
3	200	200

- (i) What is the order of the reaction with respect to X?
- (ii) Find the rate constant.
- (iii) Find the time for 75 per cent completion of the reaction.
- (iv) Find the total pressure when pressure of X is 700 mm Hg.

[IIT 2005]

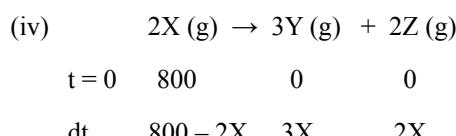
**Solution** (i) From the given data it is clear that that half life of the reaction is constant that is 100 min so it is a first order reaction.

$$(ii) k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100}$$

$$= 6.93 \times 10^{-3} \text{ min}^{-1}$$

$$(iii) t_{75\%} \text{ that is, } t_{3/4} = 2 \times t_{1/2}$$

$$= 2 \times 100 = 200 \text{ min}$$



$$\text{Total pressure} = 800 - 2X + 3X + 2X$$

$$= 800 + 3X$$

$$800 - 2X = 700$$

$$X = 50$$

$$\text{Total pressure} = 800 + 3 \times 50$$

$$= 950 \text{ mm Hg}$$

## MULTIPLE-CHOICE QUESTIONS

### Straight Objective Type Questions (Single Choice only)

1. The rate constant of a reaction depends on
  - a. Extent of reaction
  - b. Time of reaction
  - c. Temperature
  - d. Initial concentration of the reactants
2. A plot of  $1/[BrO^-]$  vs time is linear for the reaction:  

$$3BrO^- \text{ (aq)} \rightarrow BrO_3^- \text{ (aq)} + 2Br^- \text{ (aq)}$$

What is the order of the reaction with respect to the hypobromite ion,  $BrO^-$ ?

  - a. One
  - b. Two
  - c. Three
  - d. Four
3. The specific rate constant of a first order reaction depends on the
  - a. temperature
  - b. time
  - c. concentration of the reactant
  - d. concentration of the product
4. For a zeroth-order reaction:  $C \rightarrow \text{products}$ ,  $-\Delta[C]/\Delta t = k$ , which of the following graphs would be expected to give a straight line?
  - a.  $[C]^2$  vs  $t$
  - b.  $[C]$  vs  $t$
  - c.  $\ln [C]$  vs  $t$
  - d.  $1/[C]$  vs  $t$
5. For the zeroth-order reaction:  $A \rightarrow \text{products}$ , what will happen to the rate of reaction if the concentration  $A$  is doubled?
  - a. The rate will be doubled
  - b. The rate will be halved
  - c. The rate will remain the same
  - d. The rate will be quadrupled
6.  $3A \rightarrow 2B$ , rate of reaction  $+d(B)$  is equal to  $dt$ 
  - a.  $-\frac{3}{2} \frac{d[A]}{dt}$
  - b.  $-\frac{2}{3} \frac{d[A]}{dt}$
  - c.  $-\frac{1}{3} \frac{d[A]}{dt}$
  - d.  $+2 \frac{d[A]}{dt}$
7. The elementary reaction:  

$$2HI \rightarrow H_2 + I_2$$
, is an example of a \_\_\_\_\_ reaction.

- a. Tetramolecular
- b. Termolecular
- c. Bimolecular
- d. Unimolecular
8. Activation energy of a chemical reaction can be determined by
  - a. evaluating rate constant at standard temperature
  - b. evaluating velocities of reaction at two different temperatures
  - c. evaluating rate constants at two different temperatures
  - d. changing concentration of reactants
9. The elementary reaction representing the formation of ozone:  

$$O_2 \text{ (g)} + O \text{ (g)} + M \text{ (g)} \rightarrow O_3 \text{ (g)} + M^* \text{ (g)}$$

is an example of \_\_\_\_\_ reaction.

  - a. Tetramolecular
  - b. Termolecular
  - c. Bimolecular
  - d. Unimolecular
10. Catalyst is a substance which
  - a. supplies energy to the reaction
  - b. increases the equilibrium concentration of the product
  - c. changes the equilibrium constant of the reaction
  - d. shortens the time to each equilibrium
11. Which statement below regarding the half-life of a second order reaction is true?
  - a. The length of the half life remains unchanged throughout the course of the reaction.
  - b. Each half life is four times as long as the preceding one.
  - c. Each half life is half as long as the preceding one.
  - d. Each half life is twice as long as the preceding one.
12. Graph between  $\log_{10} k$  and  $(1/T)$  is linear of slope S. Hence  $E_a$  is
 

<b>a. <math>R \times S</math></b>	<b>b. <math>S/R</math></b>
<b>c. <math>R/S</math></b>	<b>d. <math>2.303 RS</math></b>
13. For a first order reaction, the half life period is independent of

- a. initial concentration  
 b. cube root of initial concentration  
 c. first power of final concentration  
 d. square root of final concentration

14. The rate of a certain hypothetical reaction  
 $A + B + C \rightarrow \text{Products}$  is given by

$$r = -\frac{d[A]}{dt} = k [A]^{1/2} [B]^{1/3} [C]^{1/4}$$

The order of the reaction is

- a. 13/12                  b. 13/14  
 c. 12/13                  d. 13/11

15.  $3A \rightarrow B + C$

It would be a zero order reaction when:

- a. the rate of reaction is proportional to square of concentration of A  
 b. the rate of reaction remains same at any concentration of A  
 c. the rate remains unchanged at any concentration of B and C  
 d. the rate of reaction doubles if concentration of B is increased to double

16. What will be initial rate of a reaction if its constant is  $10^{-3} \text{ min}^{-1}$  and the concentration of reactant is 0.2 mol dm<sup>-3</sup>?

- a. 0.02 mol dm<sup>-3</sup> min<sup>-1</sup>  
 b. 0.002 mol dm<sup>-3</sup> min<sup>-1</sup>  
 c. 0.0002 mol dm<sup>-3</sup> min<sup>-1</sup>  
 d. 2 mol dm<sup>-3</sup> min<sup>-1</sup>

17. For an endothermic reaction, where  $\Delta H$  represents the enthalpy of the reaction in kJ/mole. The minimum value for the energy of activation will be

- a. less than  $\Delta H$   
 b. zero  
 c. more than  $\Delta H$   
 d. equal to  $\Delta H$

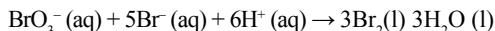
18. The rate of a gaseous reaction is given by the expression  $k[A][B]$ . If the volume of the reaction vessel is suddenly reduced to 1/4th of the initial volume, the reaction rate relating to original rate will be

- a. 8                  b. 16  
 c. 1/8                  d. 1/10

19. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are  $3.0 \times 10^{-4} \text{ s}^{-1}$ , 104.4 kJ mol<sup>-1</sup> and  $6 \times 10^{14} \text{ s}^{-1}$  respectively. The value of the rate constant as  $T \rightarrow \infty$  is

- a.  $2.0 \times 10^{18} \text{ s}^{-1}$                   b.  $6.0 \times 10^{14} \text{ s}^{-1}$   
 c. infinity                  d.  $3.6 \times 10^{30} \text{ s}^{-1}$

20. In the following reaction, how is the rate of appearance of the underlined product related to the rate of disappearance of the underlined reactant?



a.  $\frac{d[\text{Br}_2]}{dt} = -\frac{5}{3} \frac{d[\text{Br}^-]}{dt}$

b.  $\frac{d[\text{Br}_2]}{dt} = -\frac{d[\text{Br}^-]}{dt}$

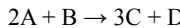
c.  $\frac{d[\text{Br}_2]}{dt} = -\frac{d[\text{Br}^-]}{dt}$

d.  $\frac{d[\text{Br}_2]}{dt} = -\frac{3}{5} \frac{d[\text{Br}^-]}{dt}$

21. The rate constant of a first order reaction,  $A \rightarrow \text{products}$ , is  $60 \times 10^{-4} \text{ s}^{-1}$ . Its rate at  $[A] = 0.01 \text{ mol l}^{-1}$  would be

- a.  $60 \times 10^{-6} \text{ mol l}^{-1} \text{ min}^{-1}$   
 b.  $36 \times 10^{-4} \text{ mol l}^{-1} \text{ min}^{-1}$   
 c.  $60 \times 10^{-2} \text{ mol l}^{-1} \text{ min}^{-1}$   
 d.  $36 \times 10^{-1} \text{ mol l}^{-1} \text{ min}^{-1}$

22. For the reaction,



Which of the following does not express the reaction rate?

- a.  $\frac{d[\text{D}]}{dt}$                   b.  $-\frac{d[\text{A}]}{2 dt}$   
 c.  $-\frac{d[\text{C}]}{3 dt}$                   d.  $-\frac{d[\text{B}]}{dt}$

23. The rate of a first order reaction is  $1.5 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$  at 0.5 M concentration of the reactant. The half-life of the reaction is

- a. 0.383 hour                  b. 23.1 min  
 c. 8.73 min                  d. 7.53 min

24. The temperature dependence of rate constant ( $k$ ) of a chemical reaction is written in terms of Arrhenius equation,  $k = A \cdot e^{-E^*/RT}$ . Activation energy ( $E^*$ ) of the reaction can be calculated by plotting

- a.  $\log k$  vs  $T^{-1}$                   b.  $\log k$  vs  $\frac{1}{\log T}$   
 c.  $k$  vs  $T$                   d.  $k$  vs  $\frac{1}{T}$

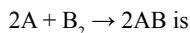
25. For the reaction,

$2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ , rate and rate constant are  $1.02 \times 10^{-4}$  and  $3.4 \times 10^{-5} \text{ sec}^{-1}$  respectively then concentration of  $\text{N}_2\text{O}_5$  at that time will be

- a. 1.732                  b. 3  
 c.  $3.4 \times 10^5$                   d.  $1.02 \times 10^{-4}$

## 7.26 ■ Chemical Kinetics

26. The experimental data for the reaction



Exp.	[A]	[B <sub>2</sub> ]	Rate(Ms <sup>-1</sup> )
1	0.50 M	0.50 M	$1.6 \times 10^{-4}$
2	0.50 M	1.00 M	$3.2 \times 10^{-4}$
3	1.00 M	1.00 M	$3.2 \times 10^{-4}$

the rate equation for the above data is

- a. rate = k[B<sub>2</sub>]
- b. rate = k[B<sub>2</sub>]<sup>2</sup>
- c. rate = k[A]<sup>2</sup>[B]<sup>2</sup>
- d. rate = k[A]<sup>2</sup>[B]

27. If the rate of the reaction is equal to the rate constant, the order of the reaction is

- a. 3
- b. 0
- c. 1
- d. 2

28. The reaction A → B follows first order kinetics. The time taken for 0.8 mole of A to produce 0.6 mole of B is 1 hour. What is the time taken for conversion of 0.9 mole of A to produce 0.675 mole of B?

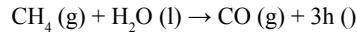
- a. 2 hours
- b. 1 hour
- c. 0.5 hour
- d. 0.25 hour

29. In a first order reaction A → B if k is rate constant and initial concentration of the reactant A is 0.5 M then the half life is

- a.  $0.693/0.5k$
- b.  $\log 2/k$
- c.  $\log 2/k \sqrt{0.5}$
- d.  $\ln 2/k$

30. Molecular hydrogen can be made from methane gas by the reaction below. How is the rate of disappearance of CH<sub>4</sub> related to the rate of appearance of H<sub>2</sub>?

$$\frac{\Delta [CH_4]}{\Delta t} = ?$$



- a.  $+3 \frac{\Delta [H_2]}{\Delta t}$
- b.  $+\frac{\Delta [H_2]}{\Delta t}$
- c.  $+\frac{1\Delta [H_2]}{3 \Delta t}$

- d. None of these

31. Methanol can be produced by the following reaction:



How is the rate of disappearance of hydrogen gas related to the rate of appearance of methanol?

$$-\frac{\Delta [H_2]}{\Delta t} = ?$$

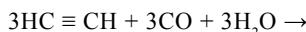
$$a. +\frac{2 \Delta [CH_3OH]}{\Delta t}$$

$$b. +\frac{1\Delta [CH_3OH]}{2 \Delta t}$$

$$c. +\frac{\Delta [H_4]}{\Delta t}$$

- d. None of these

32. Hydroquinone, HO-C<sub>6</sub>H<sub>4</sub>-OH, can be formed by the reaction with acetylene below:



How is the rate of disappearance of acetylene (HC ≡ CH) related to the appearance of hydroquinone (Hq)?

$$-\frac{\Delta [HC \equiv CH]}{\Delta t} = ?$$

$$a. +\frac{2 \Delta [Hq]}{3 \Delta t}$$

$$b. +\frac{3 \Delta [Hq]}{2 \Delta t}$$

$$c. +\frac{\Delta [Hq]}{\Delta t}$$

$$d. +\frac{1 \Delta [Hq]}{2 \Delta t}$$

33. The reaction that occurs in a Breathalyzer, a device used to determine the alcohol level in a person's blood stream, is given below. If the rate of appearance of Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> is 1.24 mol/min at a particular moment, what is the rate of disappearance of C<sub>2</sub>H<sub>6</sub>O at the moment?



- a. 1.86 mol/min
- b. 2.75 mol/min
- c. 3.86 mol/min
- d. 0.86 mol/min

34. The decomposition of dinitrogen pentoxide is described by the chemical equation



If the rate of disappearance of N<sub>2</sub>O<sub>5</sub> is equal to 1.40 mol/min at a particular moment, what is the rate of appearance of NO<sub>2</sub> at the moment?

- a. 1.80 mol/min
- b. 3.40 mol/min
- c. 0.800 mol/min
- d. 2.80 mol/min

35. The decomposition of dinitrogen pentoxide is described by the chemical equation



If the rate of appearance of  $\text{NO}_2$  is equal to 0.560 mol/min at a particular moment, what is the rate of appearance of  $\text{O}_2$  at that moment?

- a. 2.70 mol/min
- b. 3.40 mol/min
- c. 0.140 mol/min
- d. 1.14 mol/min

36. The decomposition of dinitrogen pentoxide is described by the chemical equation



If the rate of appearance of  $\text{O}_2$  is equal to 2.40 mol/min at a particular moment, what is the rate of disappearance of  $\text{N}_2\text{O}_5$  at that moment?

- a. 3.48 mol/min
- b. 4.80 mol/min
- c. 2.40 mol/min
- d. 1.80 mol/min

37. Which statement is true for the general rate law:

$$\text{Rate} = k [\text{A}]^m [\text{B}]^n?$$

- a. The exponents in the rate law must be positive integers.
- b. The values for the exponents must be determined by experiment.
- c. It can be written from the stoichiometry of the overall reaction.
- d. The overall order of the reaction is equal to 'm' times 'n'.

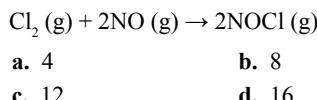
38. For a reaction that follows the general rate law, Rate =  $k [\text{A}] [\text{B}]^2$ , what will happen to the rate of reaction if the concentration of A is increased by a factor of 3.00? The rate will

- a. Increase by a factor of 6.00.
- b. Decrease by a factor of 1/6.00.
- c. Decrease by a factor of 1/3.00.
- d. Increase by a factor of 3.00.

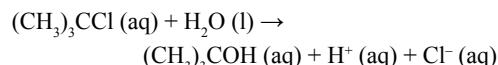
39. For a reaction that follows the general rate law, Rate =  $k [\text{A}] [\text{B}]^2$ , what will happen to the rate of reaction if the concentration of B is increased by a factor of 2.00? The rate will

- a. Increase by a factor of 4.00.
- b. Increase by a factor of 2.00.
- c. Decrease by a factor of 1/4.00.
- d. Decrease by a factor of 1/2.00.

40. The reaction between chlorine and nitric oxide to form nitrosyl chloride is shown below. If the reaction rate doubles when the concentration of  $\text{Cl}_2$  is doubled and the rate quadruples when the concentration of NO is doubled, by what factor will the rate increase if both concentrations, NO and  $\text{Cl}_2$  are doubled?



41. The hydrolysis of tert-butyl chloride is given in the reaction below:



If the rate law is: Rate =  $k [(\text{CH}_3)_3\text{CCl}]$ , what is the order of the reaction with respect to water?

- a. First
- b. Second
- c. Third
- d. Zero

42. Given the following hypothetical reaction:



If the rate law is: Rate =  $k [\text{E}]^2 [\text{F}]^{-1}$ , what is the order of reaction with respect to E?

- a. First
- b. Second
- c. Third
- d. Fourth

43. Given the following hypothetical reaction:



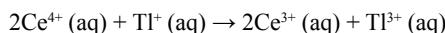
If the rate law is: Rate =  $k [\text{E}]^2 [\text{F}]^{-1}$ , What is the overall order of reaction?

- a. First
- b. Second
- c. Third
- d. Zero

44. The decomposition of ammonia to nitrogen and hydrogen on a tungsten filament at 800°C is independent of the concentration of ammonia at high pressures of ammonia. What is the order of the reaction with respect to ammonia?

- a. First
- b. Second
- c. Third
- d. Zero

45. Cerium (IV) ion reacts with thallium (I) ion in a one-step reaction shown below:

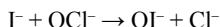


## 7.28 ■ Chemical Kinetics

If the rate law is: Rate =  $k [Ce^{4+}]^2 [Tl^+]$ , What is the overall order of the reaction?

- a. Zero
- b. First
- c. Second
- d. Third

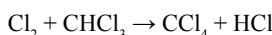
46. Iodide and hypochlorite ion react in aqueous solution according to the reaction below:



If the concentration of  $OH^-$  in the solution is doubled, the rate of the reaction is halved. What is the order of the reaction with respect to  $OH^-$ ?

- a. +2
- b. +1
- c. -2
- d. -1

47. Chlorine reacts with chloroform according to the reaction given below:



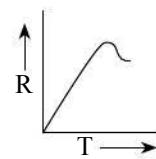
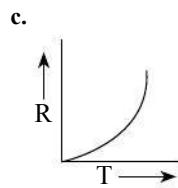
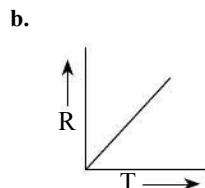
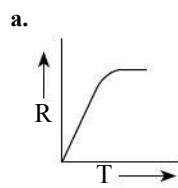
When the initial concentration of  $Cl_2$  is doubled the reaction rate increases by a factor of 1.41. What is the order of the reaction with respect to  $Cl_2$ ?

- a.  $\frac{1}{2}$
- b.  $-\frac{1}{2}$
- c. -1
- d. 2

48. If the units for rate are  $M\ s^{-1}$ , what are the units for the rate constant ( $k$ ), if the overall order of the reaction is three?

- a.  $M^{-1}\ s^{-1}$
- b.  $M^{-2}\ s^{-1}$
- c.  $s^{-1}$
- d.  $M^2\ s^{-1}$

49. Which curve corresponds to the temperature dependence of the rate  $R$  of a simple one-step reaction?



50. For a particular first order reaction, it takes 48 minutes for the concentration of the reactant to decrease to 25% of its initial value. What is the value for rate constant (in  $s^{-1}$ ) for the reaction?

- a.  $2.4 \times 10^{-4}\ s^{-1}$
- b.  $1.8 \times 10^{-3}\ s^{-1}$
- c.  $3.18 \times 10^{-4}\ s^{-1}$
- d.  $4.8 \times 10^{-4}\ s^{-1}$

51. The first order reaction,

$SO_2Cl_2 \rightarrow SO_2 + Cl_2$ , has a rate constant equal to  $2.20 \times 10^{-5}\ s^{-1}$  at 593 K. What percentage of the initial amount of  $SO_2Cl_2$  will remain after 2.00 hours?

- a. 45.8 %
- b. 85.4 %
- c. 15.4 %
- d. 75.6 %

52. The first order reaction,

$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$ , has a rate constant equal to  $0.76\ s^{-1}$  at 1000 K. How long will it take for the concentration of  $N_2O$  to decrease to 42 % of its initial concentration?

- a. 3.1 s
- b. 0.18 s
- c. 1.1 s
- d. 2.4 s

53. The isomerization reaction,

$CH_3NC \rightarrow CH_3CN$ , is first order and the rate constant is equal to  $0.46\ s^{-1}$  at 600 K. What is the concentration of  $CH_3NC$  after 0.20 minutes if the initial concentration is 0.10 M?

- a.  $14.0 \times 10^{-4}\ M$
- b.  $4.0 \times 10^{-4}\ M$
- c.  $2.4 \times 10^{-4}\ M$
- d.  $6.4 \times 10^{-4}\ M$

54. The following reaction is first order:

$C_2H_6 \rightarrow 2CH_3$ . If the rate constant is equal to  $5.5 \times 10^{-4}\ s^{-1}$  at 1000 K, how long will it take for 0.35 mol of  $C_2H_6$  in a 1.00 L container to decrease to 0.10 mol in the same container?

- a. 38 min
- b. 26 min
- c. 19 min
- d. 68 min

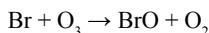
55. The decomposition of cyclopropane, was observed at  $500^\circ C$  and its concentration was monitored as a function of time. The data set is given below. What is the order of the reaction with respect to cyclopropane?

Time (hour)	[Cyclopropane], M
0	$1.00 \times 10^{-2}$

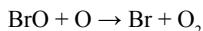
- 2                    $1.38 \times 10^{-3}$   
 4                    $1.91 \times 10^{-4}$   
 6                    $2.63 \times 10^{-5}$
- a. First           b. Second  
 c. Third          d. Zero
56. The rate constant ( $k$ ) for a first order reaction is equal to  $4.2 \times 10^{-4} \text{ s}^{-1}$ . What is the half life for the reaction?
- a.  $3.7 \times 10^3 \text{ s}$   
 b.  $7.1 \times 10^3 \text{ s}$   
 c.  $2.71 \times 10^3 \text{ s}$   
 d.  $1.7 \times 10^3 \text{ s}$
57. Acetaldehyde decomposes at 750 K:  
 $\text{CH}_3\text{CHO} \rightarrow \text{CO} + \text{CH}_4$ . The reaction is first order in acetaldehyde and the half life of the reaction is found to be 530 seconds. What is the rate constant for the reaction at this temperature?
- a.  $3.7 \times 10^{-3} \text{ s}^{-1}$   
 b.  $3.13 \times 10^3 \text{ s}^{-1}$   
 c.  $1.3 \times 10^{-3} \text{ s}^{-1}$   
 d.  $2.3 \times 10^{-3} \text{ s}^{-1}$
58. The first order reaction,  
 $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$ , has a half life of 8.75 hours at 593 K. How long will it take for the concentration of  $\text{SO}_2\text{Cl}_2$  to fall to 12.5% of its initial value?
- a. 6.24 hours  
 b. 26.2 hours  
 c. 16.2 hours  
 d. 22.6 hours
59. For the first order reaction,  
 $2\text{N}_2\text{O}(\text{g}) \rightarrow 2\text{N}_2(\text{g}) + \text{O}_2(\text{g})$ , what is the concentration of  $\text{N}_2\text{O}$  after 3 half-lives if 0.15 mol of  $\text{N}_2\text{O}$  is initially placed into a 1.00 litre reaction vessel?
- a.  $9.1 \times 10^{-2} \text{ M}$   
 b.  $0.9 \times 10^{-2} \text{ M}$   
 c.  $2.68 \times 10^{-2} \text{ M}$   
 d.  $1.9 \times 10^{-2} \text{ M}$
60. Carbon-14, which is present in all living tissue, radioactively decays via a first order process. A one-gram sample of wood taken from a living tree gives a rate for carbon-14 decay of 13.6 counts per minute. If the half-life for carbon-14 is 5720 years. How old is a wood sample that gives a rate for carbon-14 decay of 3.9 counts per minute?
- a.  $1.0 \times 10^4 \text{ years}$   
 b.  $2.1 \times 10^3 \text{ years}$   
 c.  $5.4 \times 10^3 \text{ years}$   
 d.  $3.0 \times 10^4 \text{ years}$
61. Fluorine-18 is an isotope used in Positron Emission Tomography (PET) to scan the brain. If a researcher has  $1.50 \mu\text{g}$  of  $^{18}\text{F}$ , how long before it decays to 1.0 ng? The half-life of  $^{18}\text{F}$  is 109.8 minutes.
- a.  $2.9 \times 10^{-2} \text{ hours}$   
 b. 91 hours  
 c. 39 hours  
 d. 19 hours
62. The second order reaction,  
 $2\text{Mn}(\text{CO})_5 \rightarrow \text{Mn}_2(\text{CO})_{10}$  has a rate constant equal to  $3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  at  $25^\circ\text{C}$ . If the initial concentration of  $\text{Mn}(\text{CO})_5$  is  $1.0 \times 10^{-5} \text{ M}$ , how long will it take for 90 % of the reactant to disappear?
- a.  $3.0 \times 10^{-4} \text{ s}$   
 b.  $3.9 \times 10^{-6} \text{ s}$   
 c.  $3.0 \times 10^4 \text{ s}$   
 d.  $4.3 \times 10^{-3} \text{ s}$
63. The reaction:  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ , is second order and the rate constant at  $800 \text{ K}$  is  $9.70 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ . How long will it take for  $8.00 \times 10^{-2} \text{ mol/litre}$  of HI to decrease to one-fourth of its initial concentration?
- a. 587 s  
 b. 387 s  
 c. 148 s  
 d. 687 s
64. For the hypothetical second order reaction:  
 $\text{A} \rightarrow \text{Products}$ , the general rate law is: Rate =  $k [\text{A}]^2$ . How long is the third half life of the reaction if  $[\text{A}]_0$  is  $0.080 \text{ M}$  and the first half life is 22 minutes.
- a. 48 min  
 b. 66 min  
 c. 88 min  
 d. 78 min
65. A mechanism for a naturally occurring reaction that destroys ozone is:
- Step I:  
 $\text{O}_3(\text{g}) + \text{HO}(\text{g}) \rightarrow \text{HO}_2(\text{g}) + \text{O}_2(\text{g})$
- Step II:  
 $\text{HO}_2(\text{g}) + \text{O}(\text{g}) \rightarrow \text{HO}(\text{g}) + \text{O}_2(\text{g})$
- Which species is an intermediate?
- a. O                   b.  $\text{O}_3$   
 c. HO                d.  $\text{HO}_2$
66. The decomposition of ozone in the stratosphere can occur by the following two-step mechanism:

## 7.30 ■ Chemical Kinetics

Step I:



Step II:

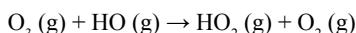


Which species is an intermediate in this mechanism?

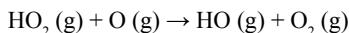
- a. BrO
- b. Br
- c. O<sub>3</sub>
- d. O

67. A mechanism for a naturally occurring reaction that destroys ozone is

Step I:



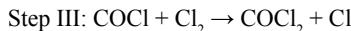
Step II:



What is the molecularity of the overall reaction?

- a. Bimolecular
- b. Unimolecular
- c. None of these because molecularity only refers to elementary steps
- d. None of these because molecularity is the difference of the exponents in the rate law

68. A three-step mechanism has been suggested for the formation of carbonyl chloride:



Which species is an intermediate in the mechanism?

- a. COCl<sub>2</sub>
- b. COCl
- c. Cl
- d. CO

69. A gas molecule at 298 K and 1 atm pressure undergoes a collision with another gas molecule approximately \_\_\_\_ seconds.

- a.  $10^{-3}$
- b.  $10^{-6}$
- c.  $10^{-9}$
- d.  $10^{-12}$

70. What fraction of collisions will have sufficient energy to react for gas whose activation energy is 68 kJ/mol at 25°C?

- a.  $2.4 \times 10^{-6}$
- b.  $6.2 \times 10^{-12}$

c.  $1.2 \times 10^4$

d.  $1.2 \times 10^{-12}$

71. When the temperature of a gas whose activation energy is 55 kJ/mol is increased from 300 K to 320 K, the fraction of collisions with sufficient energy to react

- a. Increases by a factor of 4.
- b. Increases by a factor of 2
- c. Decrease by a factor of 4
- d. Decrease by a factor of 2.

72. A common rule of thumb in organic chemistry is that increasing the temperature of a reaction at room temperature by 10°C doubles the rate. Calculate Ea for a reaction that follows this rule of thumb. Assume room temperature is 25°C.

- a. 0.597
- b. 15.2
- c. 52.9
- d. 45.9

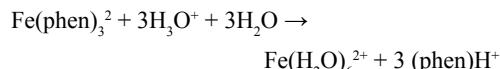
73. Consider a bimolecular reaction in the gas phase. Which one of the following changes in conditions will not cause an increase in the rate of the reaction?

- a. Increase the volume at constant temperature.
- b. Increase the temperature at constant volume
- c. Add a catalyst
- d. All of the above will increase the rate of reaction

74. The reaction for the decomposition of dinitrogen monoxide gas to form an oxygen radical is:  $\text{N}_2\text{O}(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{O}(\text{g})$ . If the activation energy is 250 kJ/mol and the frequency factor is  $8.0 \times 10^{11} \text{ s}^{-1}$ , what is the rate constant for the first order reaction at 1000 K?

- a.  $7.0 \times 10^{-2} \text{ s}^{-1}$
- b.  $3.7 \times 10^{-2} \text{ s}^{-1}$
- c.  $0.71 \times 10^{-3} \text{ s}^{-1}$
- d.  $9.7 \times 10^{-6} \text{ s}^{-1}$

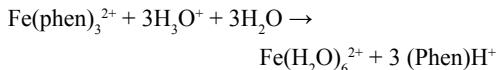
75. The aquation of tris-(1,10-phenanthroline) iron (II) in acid solution takes place according to the equation:



If the activation energy is 126 kJ/mol and frequency factor is  $8.62 \times 10^{17} \text{ s}^{-1}$ , at what temperature is the rate constant equal to  $3.63 \times 10^{-3} \text{ s}^{-1}$  for the first order reaction?

- a. 0°C
- b. 50°C
- c. 45°C
- d. 90°C

76. The equation tris(1, 10-phenanthroline) iron(II) in acid solution takes place according to the equation:



If the activation energy (Ea) is 126 kJ/mol and the rate constant at 30°C is  $9.8 \times 10^{-3} \text{ min}^{-1}$ , what is the frequency factor (A)?

- a.  $9.5 \times 10^{18} \text{ min}^{-1}$
- b.  $2.5 \times 10^{19} \text{ min}^{-1}$
- c.  $55 \times 10^{19} \text{ min}^{-1}$
- d.  $5.0 \times 10^{19} \text{ min}^{-1}$

77. The first order isomerization reaction:

Cyclopropane → Propene, has a rate constant of  $1.10 \times 10^{-4} \text{ s}^{-1}$  at 470°C and  $5.70 \times 10^{-4} \text{ s}^{-1}$  at 500°C. What is the activation energy (Ea) for the reaction?

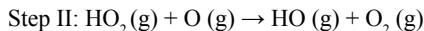
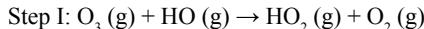
- a. 340 kJ/mol
- b. 260 kJ/mol
- c. 160 kJ/mol
- d. 620 kJ/mol

78. The first order isomerisation reaction:

Cyclopropane → propene, has a rate constant of  $1.10 \times 10^{-4} \text{ s}^{-1}$  at 470°C and an activation energy of 264 kJ/mol. What is the temperature of the reaction when the rate constant is equal to  $4.36 \times 10^{-3} \text{ s}^{-1}$ ?

- a. 240°C
- b. 150°C
- c. 540°C
- d. 450°C

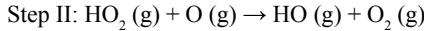
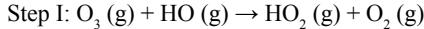
79. A mechanism for a naturally occurring reaction that destroys ozone is:



Which species is a catalyst?

- |                  |                 |
|------------------|-----------------|
| a. O             | b. $\text{O}_3$ |
| c. $\text{HO}_2$ | d. HO           |

80. A mechanism for a naturally occurring reaction that destroys ozone is



Which species is a catalyst and what type of catalysis is occurring?

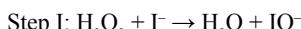
- a.  $\text{HO}_2$ , heterogeneous
- b.  $\text{HO}_2$ , homogeneous
- c. HO, homogeneous
- d. HO, heterogeneous

### Brainteasers Objective Type Questions (Single choice only)

81. The decomposition of hydrogen peroxide is given by the following reaction:



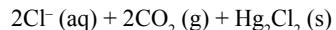
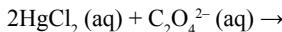
In the presence of KI the reaction is thought to occur by the following mechanism:



What is the role of  $\text{I}^-$  in this mechanism?

- a. Intermediate
- b. Transition state
- c. Catalyst
- d. Frequency factor

82. The following set of data was obtained by the method of initial rates for the reaction:



What is the rate law for the reaction?

$[\text{HgCl}_2], \text{M}$	$[\text{C}_2\text{O}_4^{2-}], \text{M}$	Rate, M/s
0.10	0.10	$1.3 \times 10^{-7}$
0.10	0.20	$5.2 \times 10^{-7}$
0.20	0.20	$1.0 \times 10^{-6}$

- a. Rate =  $k [\text{HgCl}_2] [\text{C}_2\text{O}_4^{2-}]^2$

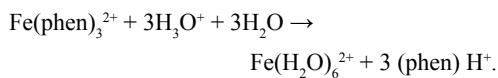
- b. Rate =  $k [\text{HgCl}_2]^2 [\text{C}_2\text{O}_4^{2-}]$

- c. Rate =  $k [\text{HgCl}_2] [\text{C}_2\text{O}_4^{2-}]^2$

- d. Rate =  $k [\text{HgCl}_2] [\text{C}_2\text{O}_4^{2-}]^{-1}$

## 7.32 ■ Chemical Kinetics

83. Which of the following statements are true about reaction mechanisms?
- A rate law can be written from the molecularity of the slowest elementary step.
  - The final rate law can include intermediates.
  - The rate of the reaction is dependent on the fastest step in the mechanism.
  - A mechanism can never be proven to be the correct pathway for a reaction.
- I and II
  - I and IV
  - II and III
  - I, II and III
84. The data given below is for the reaction of NO and  $\text{Cl}_2$  to form  $\text{NOCl}$  at 295 K
- What is the rate law?
- | $[\text{Cl}_2]$ | [NO] | Initial rate<br>(mol $\text{l}^{-1} \text{s}^{-1}$ ) |
|-----------------|------|------------------------------------------------------|
| 0.05            | 0.05 | $1 \times 10^{-3}$                                   |
| 0.15            | 0.05 | $3 \times 10^{-3}$                                   |
| 0.05            | 0.15 | $9 \times 10^{-3}$                                   |
- $r = k [\text{NO}] [\text{Cl}_2]$
  - $r = k [\text{Cl}_2]^1 [\text{NO}]^2$
  - $r = k [\text{Cl}_2]^2 [\text{NO}]$
  - $r = k [\text{Cl}_2]^1$
85. The following set of data was obtained by the method of initial rates for the reaction:
- $$2\text{HgCl}_2(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}) \rightarrow 2\text{Cl}^-(\text{aq}) + 2\text{CO}_2(\text{g}) + \text{Hg}_2\text{Cl}_2(\text{s})$$
- | $[\text{HgCl}_2], \text{M}$ | $[\text{C}_2\text{O}_4^{2-}], \text{M}$ | Rate, M/s            |
|-----------------------------|-----------------------------------------|----------------------|
| 0.10                        | 0.10                                    | $1.3 \times 10^{-7}$ |
| 0.10                        | 0.20                                    | $5.2 \times 10^{-7}$ |
| 0.20                        | 0.20                                    | $1.0 \times 10^{-6}$ |
- What is the value of the rate constant,  $k$ ?
- $1.6 \times 10^{-4} \text{ M}^2 \cdot \text{s}$
  - $1.3 \times 10^{-4} \text{ M}^2 \cdot \text{s}$
  - $1.4 \times 10^{-7} \text{ M}^2 \cdot \text{s}$
  - $1.3 \times 10^{-6} \text{ M}^2 \cdot \text{s}$
86. The equation of tris(1,10-phenanthroline) iron(II) in acid solution takes place according to the equation:



If the activation energy ( $E_a$ ) is 126 kJ/mol and the rate constant at 30°C is  $9.8 \times 10^{-3} \text{ min}^{-1}$ , what is the rate constant at 50°C?

- $2.2 \times 10^{-1} \text{ min}^{-1}$
- $3.4 \times 10^{-2} \text{ min}^{-1}$
- $0.23 \times 10^{-1} \text{ min}^{-1}$
- $1.2 \times 10^{-1} \text{ min}^{-1}$

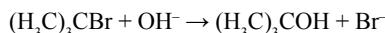
87. From the following data for the reaction between A and B

[A] mol $\text{l}^{-1}$	[B] mol	initial rate $\text{l}^{-1} \text{ s}^{-1}$ 300 K	(mol $\text{l}^{-1} \text{s}^{-1}$ ) 320 K
$2.5 \times 10^{-4}$	$3.0 \times 10^{-5}$	$5.0 \times 10^{-4}$	$2.0 \times 10^{-3}$
$5.0 \times 10^{-4}$	$6.0 \times 10^{-5}$	$4.0 \times 10^{-3}$	—
$1.0 \times 10^{-3}$	$6.0 \times 10^{-5}$	$1.6 \times 10^{-2}$	—

Calculate the rate of the equation.

- $r = k [\text{B}]^1$
- $r = k [\text{A}]^2$
- $r = k [\text{A}]^2 [\text{B}]^1$
- $r = k [\text{A}] [\text{B}]$

88. The following set of data was obtained by the method of initial rates for the reaction:



What is the order of reaction with respect to ion,  $\text{OH}^-$ ?

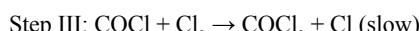
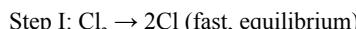
$[(\text{H}_3\text{C})_3\text{CBr}], \text{M}$	$[\text{OH}^-], \text{M}$	Initial rate, M/s
0.25	0.25	$1.1 \times 10^{-4}$
0.50	0.25	$2.2 \times 10^{-4}$
0.50	0.50	$2.2 \times 10^{-4}$

- First
- Second
- Third
- Zero

89. At 380°C, half life period for the first order decomposition of  $\text{H}_2\text{O}_2$  is 360 min. The energy of activation of the reaction is 200 kJ mol<sup>-1</sup>. Calculate the time required for 75 % decomposition at 450°C if half life for decomposition of  $\text{H}_2\text{O}_2$  is 10.17 min at 450°C.

- 20.4 min
- 408 min
- 10.2 min
- none

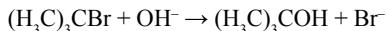
90. A three-step mechanism has been suggested for the formation of carbonyl chloride:



What is the molecularity of the rate-determining step?

- Termolecular
- Unimolecular
- Bimolecular
- None of these

91. The following set of data was obtained by the method of initial rates for the reaction:



What is the rate of the reaction?

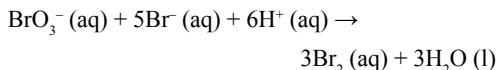
$[(H_3C)_3CBr], M$	$[OH^-], M$	Initial rate, M/s
0.25	0.25	$1.1 \times 10^{-4}$
0.50	0.25	$2.2 \times 10^{-4}$
0.50	0.50	$2.2 \times 10^{-4}$

- $4.4 \times 10^{-4} s^{-1}$
- $2.4 \times 10^{-4} s^{-1}$
- $14.0 \times 10^{-4} s^{-1}$
- $3.14 \times 10^{-4} s^{-1}$

92. For a first reaction A → B, the reaction rate at reactant concentration of 0.01 M is found to be  $2.0 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$ . The half life period of the reaction is

- 220 s
- 30 s
- 300 s
- 347 s

93. The following set of data was obtained by the method of initial rates for the reaction:

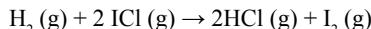


Calculate the initial rate when  $BrO_3^-$  is 0.30 M,  $Br^-$  is 0.050 M and  $H^+$  is 0.15 M.

$[BrO_3^-], M$	$[Br^-], M$	$[H^+], M$	Rate, M/s
0.10	0.10	0.10	$8.0 \times 10^{-4}$
0.20	0.10	0.10	$1.6 \times 10^{-3}$
0.20	0.15	0.10	$2.4 \times 10^{-3}$
0.10	0.10	0.25	$5.0 \times 10^{-3}$

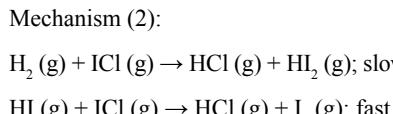
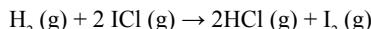
- $3.17 \times 10^{-4} \text{ M/s}$
- $6.7 \times 10^{-3} \text{ M/s}$
- $2.7 \times 10^{-3} \text{ M/s}$
- $1.71 \times 10^{-3} \text{ M/s}$

94. The reaction of hydrogen and iodine monochloride is given as:



This reaction is of first order with respect to  $H_2 (g)$  and  $ICl (g)$ , following mechanisms were proposed:

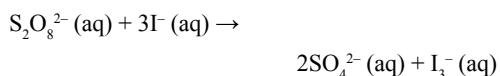
Mechanism (1):



Which of the above mechanism(s) can be consistent with the given information about the reaction?

- 2 only
- Both 1 and 2
- Neither 1 nor 2
- 1 only

95. The following set of data was obtained by the method of initial rates for the reaction:



What is the rate law for the reaction?

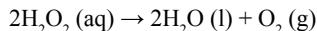
$[S_2O_8^{2-}], M$	$[I^-], M$	Initial rate, M $s^{-1}$
0.25	0.10	$9.00 \times 10^{-3}$
0.10	0.10	$3.60 \times 10^{-3}$
0.20	0.30	$2.16 \times 10^{-2}$

- Rate =  $k [S_2O_8^{2-}] [I^-]^2$
- Rate =  $k [S_2O_8^{2-}]^2 [I^-]$
- Rate =  $k [S_2O_8^{2-}] [I^-]$
- Rate =  $k [S_2O_8^{2-}] [I^-]^5$

96. If 60% of a first order reaction was completed in 60 minutes, 50 % of the same reaction would be completed in approximately

- 50 minutes
  - 45 minutes
  - 60 minutes
  - 40 minutes
- ( $\log 4 = 0.60$ ,  $\log 5 = 0.69$ )

97. Hydrogen peroxide decomposes to water and oxygen according to the reaction below:



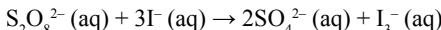
In the presence of large excesses of  $I^-$  ion, the following set of data is obtained. What is the average rate of disappearance of  $H_2O_2$  (aq) in M/s in the first 45.0 seconds of the reaction if 1.00 litre of  $H_2O_2$  reacts at 25°C and 1.00 atm pressure?

## 7.34 ■ Chemical Kinetics

Time, s	O <sub>2</sub> (g) collected, ml
0.0	0.0
45.0	2.00
90.0	4.00
135.0	6.00

- a.  $2.63 \times 10^{-4}$  M/s  
 b.  $6.33 \times 10^{-6}$  M/s  
 c.  $3.63 \times 10^{-6}$  M/s  
 d.  $1.36 \times 10^{-3}$  M/s

98. The following set of data was obtained by the method of initial rates for the reaction:

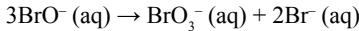


What is the initial rate when S<sub>2</sub>O<sub>8</sub><sup>2-</sup> is 0.15 M and I<sup>-</sup> is 0.15 M?

[S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ], M	[I <sup>-</sup> ], M	Initial rate, M s <sup>-1</sup>
0.25	0.10	$9.00 \times 10^{-3}$
0.10	0.10	$3.60 \times 10^{-3}$
0.20	0.30	$2.16 \times 10^{-2}$

- a.  $8.10 \times 10^{-3}$  M s<sup>-1</sup>  
 b.  $2.80 \times 10^{-4}$  M s<sup>-1</sup>  
 c.  $6.18 \times 10^{-3}$  M s<sup>-1</sup>  
 d.  $18.1 \times 10^{-3}$  M s<sup>-1</sup>

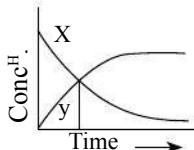
99. In aqueous solution, hypobromite ion (BrO<sup>-</sup>) reacts to produce bromate ion (BrO<sub>3</sub><sup>-</sup>), and bromide ion (Br<sup>-</sup>), according to the following chemical equation.



A plot of 1/[BrO<sup>-</sup>] vs. time is linear and the slope is equal to  $0.056 \text{ M}^{-1} \text{ s}^{-1}$ . If the initial concentration of BrO<sup>-</sup> is 0.80 M, how long will it take one-half of the BrO<sup>-</sup> ion to react?

- a. 2.12 s  
 b. 22 s  
 c. 12 s  
 d. 3.22 s

100. The accompanying figure depicts the change in concentrations of species X and Y for the reaction X → Y, as a function of time. The point of intersection of the two curves represents



- a. t<sub>1/2</sub>  
 b. t<sub>3/4</sub>  
 c. t<sub>2/3</sub>  
 d. unpredictable

101. Consider the following statements:

- (1) Rate of a process is directly proportional to its free energy change.  
 (2) The order of an elementary reaction step can be determined by examining the stoichiometry.  
 (3) The first order reaction describe exponential time coarse.

Of the statements

- a. 1 and 2 are correct  
 b. 1 and 3 are correct  
 c. 2 and 3 are correct  
 d. 1, 2 and 3 are correct

102. Hydrogen iodide decomposes at 800 K via a second order process to produce hydrogen and iodine according to the following chemical equation.



At 800 K it takes 142 seconds for the initial concentration of HI to decrease from  $6.75 \times 10^{-2}$  M to  $3.50 \times 10^{-2}$  M. What is the rate constant for the reaction at this temperature?

- a.  $6.69 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$   
 b.  $7.96 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$   
 c.  $19.6 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$   
 d.  $9.69 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$

103. A complex reaction, 2A + B → C takes place in two steps as follows:



If K<sub>1</sub> << K<sub>2</sub>, order of reaction is

- a. Zero order                    b. One  
 c. Two                            d. Three

104. When the concentration of A is doubled, the rate for the reaction: 2A + B → 2C quadruples. When the concentration of B is doubled the rate remains the same. Which mechanism below is consistent with the experimental observations?

- a. Step I: 2A ⇌ D (fast equilibrium)  
 Step II: B + D → E (slow)  
 Step III: E → 2C (fast)
- b. Step I: A + B ⇌ D (fast equilibrium)  
 Step II: A + D → 2C (slow)
- c. Step I: A + B → D (slow)  
 Step II: A + D ⇌ 2C (fast equilibrium)
- d. Step I: 2A → D (slow)  
 Step II: B + D → E (fast)  
 Step III: E → 2C (fast)

- 105.** Which of the following are the examples of pseudo-unimolecular reactions?

- Acid catalysed hydrolysis of an ester
- Inversion of cane sugar
- Decomposition of ozone
- Decomposition of  $\text{N}_2\text{O}_5$

Select the correct answers using the codes given below

- |                      |                      |
|----------------------|----------------------|
| <b>a.</b> 1 and 2    | <b>b.</b> 1 and 3    |
| <b>c.</b> 2, 3 and 4 | <b>d.</b> 1, 2 and 4 |

- 106.** For a reaction  $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$

It is observed that

$$-\frac{d[\text{NH}_3]}{dt} = K_1 (\text{NH}_3),$$

$$\frac{d[\text{N}_2]}{dt} = K_2 (\text{NH}_3),$$

$$\frac{d[\text{H}_2]}{dt} = K_3 (\text{NH}_3),$$

What is the relation between  $K_1$ ,  $K_2$  and  $K_3$ ?

- $K_1 = K_2 = K_3$
- $3K_1 = 6K_2 = 2K_3$
- $6K_1 = 3K_2 = 2K_3$
- $2K_1 = 3K_2 = 6K_3$

- 107.** The rate equation for a chemical reaction is

$$\text{Rate of reaction} = k [\text{X}] [\text{Y}]$$

Consider the following statements in this regard

- The order of reaction is one
- The molecularity of reaction is two
- The rate constant depends upon temperature

Of these statements:

- 1 and 3 are correct
- 1 and 2 are correct
- 2 and 3 are correct
- 1, 2 and 3 are correct

- 108.** Which of the following statements are correct?

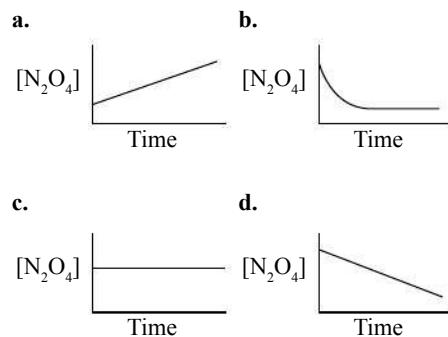
- Order of a reaction can be known from experimental results and not from the stoichiometry of reaction.
- Molecularity of a reaction refers to (i) each of the elementary steps in (an overall mechanism of) a complex reaction or (ii) a single step reaction
- Overall molecularity of a reaction may be determined in a manner similar to overall order of reaction

- (4) Overall order of a reaction  $\text{A}^m + \text{B}^n \rightarrow \text{AB}_x$  is  $m + n$ .

Select the correct answer using the following codes:

- |                      |                      |
|----------------------|----------------------|
| <b>a.</b> 2 and 3    | <b>b.</b> 1, 3 and 4 |
| <b>c.</b> 2, 3 and 4 | <b>d.</b> 1, 2 and 3 |

- 109.** Which of these graphs best describes the rate at which  $\text{N}_2\text{O}_4$  decomposes to  $\text{NO}_2$  if the reaction is of first-order?



- 110.** The following data pertains to the reaction between A and B

S. No.	[A] mol L <sup>-1</sup>	[B] mol L <sup>-1</sup>	Rate Mol L <sup>-1</sup> t <sup>-1</sup>
1	$1 \times 10^{-2}$	$2 \times 10^{-2}$	$2 \times 10^{-4}$
2	$2 \times 10^{-2}$	$2 \times 10^{-2}$	$4 \times 10^{-4}$
3	$2 \times 10^{-2}$	$4 \times 10^{-2}$	$8 \times 10^{-4}$

Which of the following inferences are drawn from the above data?

- Rate constant of the reaction is  $10^{-4}$
- Rate law of the reaction is  $k [\text{A}][\text{B}]$
- Rate of reaction increases four times by doubling the concentration of each reactant.

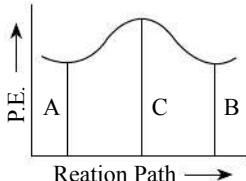
Select the correct answer using the codes given below:

- |                   |                      |
|-------------------|----------------------|
| <b>a.</b> 1 and 3 | <b>b.</b> 2 and 3    |
| <b>c.</b> 1 and 2 | <b>d.</b> 1, 2 and 3 |

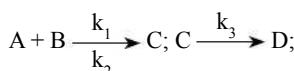
- 111.** Which of the following statements are correct about half life period?

- time required for 99.9% completion of a reaction is 100 times the half life period.
- time required for 75% completion of a 1<sup>st</sup> order reaction is double the half life of the reaction.
- average life = 1.44 times the half life for 1<sup>st</sup> order reaction
- it is proportional to initial concentration for zeroth order

## 7.36 ■ Chemical Kinetics

- a.** 1, 2 and 3      **b.** 2, 3 and 4  
**c.** 2 and 3      **d.** 3 and 4
- 112.** With respect to the figure given below which of the following statement is correct
- 
- a.**  $\Delta E$  for the forward reaction is  $C - B$   
**b.**  $\Delta E$  for the forward reaction is  $B - A$   
**c.**  $E$  (for reverse reaction) =  $C - A$   
**d.**  $E_{(Forward)} > E_{(Backward)}$
- 113.** The rate constant for the reaction,  
 $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$   
is  $3.0 \times 10^{-4} \text{ s}^{-1}$ . If start made with  $1.0 \text{ mol L}^{-1}$  of  $\text{N}_2\text{O}_5$ , calculate the rate of formation of  $\text{NO}_2$  at the moment of the reaction when concentration of  $\text{O}_2$  is  $0.1 \text{ mol L}^{-1}$ .
- a.**  $1.2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$   
**b.**  $3.6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$   
**c.**  $9.6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$   
**d.**  $4.8 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
- 114.** A gaseous compound decomposes on heating as per the following equation:  
 $\text{A(g)} \rightarrow \text{B(g)} + 2\text{C(g)}$ . After 5 minutes and 20 seconds, the pressure increases by 96 mm Hg. If the rate constant for this first order reaction is  $5.2 \times 10^{-4} \text{ s}^{-1}$ , the initial pressure of A is
- a.** 480 mm      **b.** 376 mm  
**c.** 696 mm      **d.** 313 mm
- 115.** The basic theory of Arrhenius equation is that
- Activation energy and pre exponential factors are always temperature independent
  - The number of effective collisions is proportional to the number of molecule above a certain threshold energy.
  - As the temperature increases, the number of molecules with energies exceeding the threshold energy increases.
  - The rate constant is a function of temperature
- a.** 2, 3 and 4      **b.** 1, 2 and 3  
**c.** 2 and 3      **d.** 1 and 3
- 116.** For the two gaseous reactions, following data are given  
 $\text{A} \rightarrow \text{B}; k_1 = 10^{10} e^{-20000/T}$   
 $\text{C} \rightarrow \text{D}; k_2 = 10^{12} e^{-24606/T}$   
The temperature at which  $k_1$  becomes equal to  $k_2$  is
- a.** 468 K      **b.** 1000 K  
**c.** 800 K      **d.** 1200 K  
**e.** 300 K
- 117.** The bromination of acetone that occurs in acid solution is represented by this equation.  
 $\text{CH}_3\text{COCH}_3(\text{aq}) + \text{Br}_2(\text{aq}) \rightarrow \text{CH}_3\text{COCH}_2\text{Br}(\text{aq}) + \text{H}^+(\text{aq}) + \text{Br}^-(\text{aq})$   
These kinetic data were obtained from given reaction concentrations.
- Initial concentrations, (M)
- | $[\text{CH}_3\text{COCH}_3]$ | $[\text{Br}_2]$ | $[\text{H}^+]$ |
|------------------------------|-----------------|----------------|
| 0.30                         | 0.05            | 0.05           |
| 0.30                         | 0.10            | 0.05           |
| 0.30                         | 0.10            | 0.10           |
| 0.40                         | 0.05            | 0.20           |
- Initial rate, disappearance of  $\text{Br}_2, \text{Ms}^{-1}$
- |                      |
|----------------------|
| $5.7 \times 10^{-5}$ |
| $5.7 \times 10^{-5}$ |
| $1.2 \times 10^{-4}$ |
| $3.1 \times 10^{-4}$ |
- Based on these data, the rate equation is:
- $\text{Rate} = k [\text{CH}_3\text{COCH}_3][\text{Br}_2][\text{H}^+]^2$
  - $\text{Rate} = k [\text{CH}_3\text{COCH}_3][\text{Br}_2][\text{H}^+]$
  - $\text{Rate} = k [\text{CH}_3\text{COCH}_3][\text{H}^+]$
  - $\text{Rate} = k [\text{CH}_3\text{COCH}_3][\text{Br}_2]$
- 118.** If the volume of the vessel in which the reaction  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$  is occurring is diminished to  $1/3$  rd of its initial volume. The rate of the reaction will be increased by
- a.** 5 times      **b.** 8 times  
**c.** 27 times      **d.** 35 times
- 119.** When the reactants are A, B and C at one mole per litre each the rate equation is, rate =  $k [A]^x [B]^{1/y} [C]^{x/y}$ . The order of the reaction is
- a.**  $X + \frac{(1+X)}{Y}$       **b.**  $X - Y + \frac{X}{Y}$   
**c.**  $X + Y + \frac{X}{Y}$       **d.**  $2(X + Y)$

120. For the mechanism,



The equilibrium step is fast.

The reaction rate,  $d/dt [D]$  is

- a.  $k_1 k_2 k_3 [A][B]$
- b.  $\frac{k_1 k_3}{k_2} [A] [B]$
- c.  $\frac{k_1 k_3}{k_2 + k_3} [A] [B]$
- d.  $\frac{k_2 k_3}{k_1} [A] [B]$

### Multiple Correct Answer Type Questions

121. For the reaction

$P + Q \rightarrow 2R + S$ . Which of the following statement is/are correct?

- a. Rate of disappearance of P = rate of appearance of S
- b. Rate of disappearance of P = rate of disappearance of Q
- c. Rate of disappearance of Q =  $2 \times$  rate of appearance of R
- d. Rate of disappearance of Q =  $\frac{1}{2} \times$  rate of appearance of R

122. In Arrhenius equation:  $k = A e^{-E_a/RT}$

- a. The exponential factor has the units of reciprocal of temperature.
- b. The pre-exponential factor has the units of rate of the reaction.
- c. The pre-exponential factor has the units of rate constant of the reaction.
- d. The exponential factor is a dimensionless quantity.

123. In a hypothetical reaction  $A \rightarrow B$ , the activation energy for the forward and backward reaction are 15 and 9  $\text{kJ mol}^{-1}$  respectively. The potential energy of X is 10  $\text{kJ mol}^{-1}$

- a. Heat of reaction is 6  $\text{kJ}$ .
- b. The threshold energy of the reaction is 25  $\text{kJ}$ .
- c. The potential energy of B is 16  $\text{kJ}$ .
- d. Heat of reaction is 9  $\text{kJ}$ .

124. Which of the following is/are correctly matched?

- a.  $\frac{k_{20} + T^\circ C}{kT^\circ C} = \frac{1}{4}$ ; Endothermic reaction

b.  $\frac{k_{20} + T^\circ C}{kT^\circ C} = 4$ ; Exothermic reaction

c.  $\frac{k_{10} + T^\circ C}{kT^\circ C} = 2$ ; Endothermic reaction

d.  $\frac{k_{10} + T^\circ C}{kT^\circ C} = \frac{1}{2}$ ; Exothermic reaction

125. For a first order reaction

a. Plot between 't' and  $\log_{10}(a - X)$  will be a parabola.

b.  $dx/dt = k(a - x)$

c.  $K = \frac{2.303}{t} \log_{10} \frac{a}{a - X}$

d.  $t_2 - t_1 = \frac{2.303}{k} \log_{10} \frac{a - X_1}{a - X_2}$

126. Which of the following statement is/are correct regarding a catalyst?

- a. Decreases the activation energy.
- b. Increases the average kinetic energy of reacting molecules.
- c. Increases the frequency of collision of reacting.
- d. Alters the reaction mechanism.

127. For a first order reaction, which is/are correct here?

- a. The time taken for the completion of 75 % reaction is twice the  $t_{1/2}$  of the reaction
- b. The degree of dissociation is equal to  $1 - e^{-kt}$ .
- c. A plot of reciprocal concentration of the reactant versus time gives a straight line
- d. The pre-exponential factor in the Arrhenius equation has the dimension of time,  $T^{-1}$ .

128. Which of the following statement(s) is/are incorrect?

- a. A plot of P versus  $1/V$  is linear at constant temperature.
- b. A plot of P versus  $1/T$  is linear at constant volume.
- c. A plot of  $\log K_p$  versus  $1/T$  is linear
- d. A plot of  $\log [x]$  versus time is linear for zero order reaction.

129. Which of the following are not the permitted values of molecularity?

- a. 0
- b. 2
- c. 5
- d. 1

## 7.38 ■ Chemical Kinetics

130. Which of the following reaction is/are of the first order?
- The acidic hydrolysis of ester.
  - The inversion of cane-sugar in the presence of an acid.
  - The decomposition of ammonium nitrate in an aqueous solution.
  - Formation of  $\text{NH}_3$  by Haber's Process.
131. In which of the following ways does an activated complex differ from an ordinary molecule?
- $\Delta H^\circ_f$  is probably positive.
  - It is quite unstable and has no independent existence
  - The system has no vibrational character
  - The system has a greater vibrational character
132. Which of the following is/are experimentally determined?
- Rate law
  - Order
  - Molecularity
  - Rate constant
133. For a reaction  $\text{X} \rightarrow \text{Y}$ , the rate law is  $R = k[\text{X}]^2$ , which of the following statements are correct?
- K remains constant in the reaction at all temperatures.
  - The unit of rate constant  $\text{Litre mole}^{-1} \text{s}^{-1}$ .
  - The reaction follows first order kinetics.
  - The  $t_{1/2}$  of the reaction depends upon initial concentration of reactant.
134. Which of the following is/are examples of unimolecular reactions?
- $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$
  - $\text{O}_3 \rightarrow \text{O}_2 + \text{O}$
  - $\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH}_2 \end{array} \rightarrow \text{CH}_3\text{CH} = \text{CH}_2$
  - $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$
135. Two reactions  $\text{X} \rightarrow \text{Products}$  and  $\text{Y} \rightarrow \text{products}$  have rate constant  $k_x$  and  $k_y$  at temperature T and activation energies  $E_x$  and  $E_y$  respectively. If  $k_x > k_y$  and  $E_x < E_y$  and assuming that for both the reaction is same, then
- At lower temperature  $k_y > k_x$
  - At higher temperature  $k_x$  will be greater than  $k_y$
- c. At lower temperature  $k_x$  and  $k_y$  will be close to each other in magnitude
- d. At temperature rises,  $k_x$  and  $k_y$  will be close to each other in magnitude
136. The calculation of the Arrhenius factor is based on the
- Idea that the reactant species must come together, leading to the formation of the transition state which then transforms into the products
  - Idea that, for a reaction to take place, the reactant species must come together
  - Calculation of the order of the reaction
  - Calculation of the molecularity of the reaction
137. For producing the effective collisions, the colliding molecules must possess
- Energy equal to activation energy
  - Energy equal to or greater than threshold energy
  - Proper orientation
  - Energy greater than threshold energy
138. In Arrhenius equation,  $k = A \exp(-E_a/RT)$ . A may be regarded as the rate constant at
- Very high temperature
  - Very low temperature
  - High activation energy
  - Zero activation energy
139. The basic theory behind Arrhenius's equation is that
- The activation energy and pre-exponential factor are always temperature-independent
  - The rate constant is a function of temperature
  - The number of effective collisions is proportional to the number of molecules above a certain threshold energy
  - As the temperature increases, so does the number of molecules with energies exceeding the threshold energy.
140. For a first order reaction, which of the following are not correct?
- $t_{7/8} = 2 t_{3/4}$
  - $t_{3/4} = 2 t_{1/2}$
  - $t_{15/16} = 4 t_{1/2}$
  - $t_{15/16} = 3 t_{3/4}$
141. In the formation of sulphur trioxide by the contact process,

$2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ , the rate of reaction can be measured as  $-\frac{d(\text{SO}_2)}{dt} = 6.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ .

Here the incorrect statements are

- The rate of reaction expressed in terms of  $\text{O}_2$  will be  $4.0 \times 10^{-4} \text{ mole L}^{-1} \text{ s}^{-1}$
- The rate of reaction expressed in terms of  $\text{O}_2$  will be  $6.0 \times 10^{-6} \text{ mole L}^{-1} \text{ s}^{-1}$
- The rate of reaction expressed in terms of  $\text{SO}_3$  will be  $6.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ .
- The rate of reaction expressed in terms of  $\text{O}_2$  will be  $3.0 \times 10^{-4} \text{ mole L}^{-1} \text{ s}^{-1}$

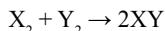
142. Which of the following expressions is/are not correct?

- $\log k = \log A - \frac{E_a}{2.303 RT}$
- $\ln A = \ln k + \frac{E_a}{RT}$
- $k Ae^{-RT/E_a}$
- $\ln k = \ln A + E_a/RT$

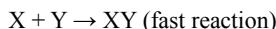
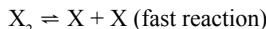
143. Which of the following are examples of pseudo-unimolecular reactions?

- $\text{CH}_3\text{COCH}_3 + \text{H}_2\text{O} \xrightarrow{\text{OH}^-} \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$
- $\text{C}_2\text{H}_5\text{COCl} + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{COOH} + \text{HCl}$
- $\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \xrightarrow{\text{OH}^+} \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$
- $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{OH}^+} \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$

144. In hypothetical reaction



Follows the mechanism as given below



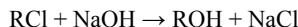
Here the correct statement is/are

- Order of reaction is 3/2.
- Molecularity is 2.
- $R = k [\text{X}] [\text{Y}_2]$
- Both molecularity and order = 3

145. Which of the following graphs for a first order reaction ( $A \rightarrow \text{Products}$ ) would be straight line?

- Rate vs time
- Rate vs  $[\text{A}]$
- Rate vs  $\log [\text{A}]$
- $\log [\text{A}]$  vs time

146. The rate law for the reaction



is given by  $\text{Rate} = k(\text{RCl})$ . The rate of the reaction is

- Halved by reducing the concentration of  $\text{RCl}$  by one half.
- Increased by increasing the temperature of the reaction.
- Remains same by change in temperature.
- Doubled by doubling the concentration of  $\text{NaOH}$ .

147. What happens when the temperature of a reaction system is increased by  $10^\circ\text{C}$ ?

- The effective number of collisions between the molecules possessing certain threshold energy increases atleast by 100%.
- The total number of collisions between reacting molecules increases atleast by 100%
- The activation energy of the reaction is increased
- The total number of collisions between reacting molecules increases merely by 1-2%.

148. Which of the following statement about the Arrhenius equation is/are correct?

- On raising temperature, rate constant of the reaction of greater activation energy increases less rapidly than that of the reaction of smaller activation energy.
- The term  $e^{-E_a/RT}$  represents the fraction of the molecules having energy in excess of threshold value.
- The pre-exponential factor becomes equal to the rate constant of the reaction at extremely high temperature.
- When the activation energy of the reaction is zero, the rate becomes independent of temperature

149. In Arrhenius equation:  $K = Ae^{-E_a/RT}$

- The pre-exponential factor has the units of rate constant of the reaction
- The exponential factor is a dimensionless quantity
- The exponential factor has the units of reciprocal of temperatures
- The pre-exponential factor has the units of rate of the reaction

150. Two reactions A → Products and B → Products have rate constants  $k_A$  and  $k_B$  at temperature T and activation energies  $E_A$  and  $E_B$  respectively. If  $k_A > k_B$  and  $E_A < E_B$  and assuming that A for both the reactions is same, then:

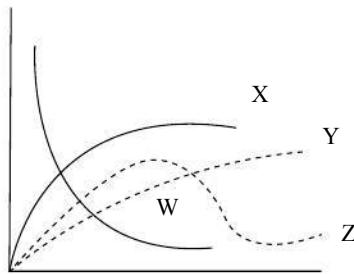
- At lower temperature  $k_A$  and  $k_B$  will be close to each other in magnitude
- At lower temperature  $k_B > k_A$
- At higher temperature  $k_A$  will be greater than  $k_B$
- As temperature rises,  $k_A$  and  $k_B$  will be close to each other in magnitude

### Linked-Comprehension Type Questions

#### Comprehension 1

The mathematical representation of a reaction is given by rate law which is experimentally determined. Order of a reaction w.r.t. any reactant is the power of its concentration shown by the rate law equation. Rate constant represents the proportionality factor in rate law equation. Both order of reaction and rate constant are determined from rate law equation. Molecularity is defined only for an elementary reaction. Molecularity can be 1, 2, 3 while order can be 0 to 3 or in fraction also.

151. For the reaction P + Q ⇌ R + S . The variation of the concentration of the products is given by the curve



152. The rate constant (k) for a reaction  $2x + y \rightarrow$  product was observed to be  $2.64 \times 10^{-6}$  litre  $\text{mol}^{-1} \text{S}^{-1}$  after 20 sec,  $2.78 \times 10^{-6}$  litre  $\text{mol}^{-1}$  after 35 sec and  $2.54 \times 10^{-6}$  litre  $\text{mol}^{-1} \text{S}^{-1}$  after 50 second. The order of the reaction is

- |                           |                            |
|---------------------------|----------------------------|
| a. Zero                   | b. I <sup>st</sup>         |
| c. II <sup>nd</sup> order | d. III <sup>rd</sup> order |

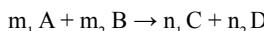
153.  $2P + 3Q + R \rightarrow$  product

If for this reaction Rate (R) =  $K [P]^{1/2} [Q]^1 [R]^{1/2}$

- The order of this reaction is
- |                     |                    |
|---------------------|--------------------|
| a. Zero             | b. I <sup>st</sup> |
| c. II <sup>nd</sup> | d. 3/2             |

#### Comprehension 2

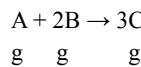
For a reaction shown as



The rate of reaction in terms of stoichiometric coefficients of reactants and products can be given as

$$\frac{dx}{dt} = \frac{-1}{m_1} \frac{d(A)}{dt} = \frac{-1}{m_2} \frac{d(B)}{dt} = \frac{1}{n_1} \frac{d(C)}{dt} = \frac{1}{n_2} \frac{d(D)}{dt}$$

154. Observe the reaction given below



If the rate of this reaction  $-\frac{dA}{dt}$  is  $2 \times 10^{-3}$  mol  $\text{lit}^{-1} \text{min}^{-1}$  than the value of  $\frac{dB}{dt}$  and  $\frac{dC}{dt}$  will be respectively

- $1 \times 10^{-3}, 2/3 \times 10^{-3}$
- $4 \times 10^{-3}, 6 \times 10^{-3}$
- $6 \times 10^{-3}, 4 \times 10^{-3}$
- $2/3 \times 10^{-3}, 1 \times 10^{-3}$

155. For the reaction  $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$  it is

$$\text{found that } -\frac{d\text{NH}_3}{dt} = K_1 (\text{NH}_3)$$

$$\frac{d\text{N}_2}{dt} = K_2 [\text{NH}_3],$$

$$\frac{d\text{H}_2}{dt} = K_3 [\text{NH}_3]$$

the correct relation between  $K_1$ ,  $K_2$  and  $K_3$  can be given as ?

- $3K_1 = 2K_2 = 6K_3$
- $6K_1 = 3K_2 = 2K_3$
- $K_1 = K_2 = K_3$
- $2K_1 = 3K_2 = 6K_3$

156. For the reaction  $W + X \rightarrow Y + Z$  , the rate ( $dx/dt$ ) when plotted against time 't' gives a straight line parallel to time axis. The order and rate for this reaction are

- |            |           |
|------------|-----------|
| a. O, K    | b. 1, K+1 |
| c. II, K+1 | d. K, K+1 |

157. For this reaction  $\text{X}^- + \text{OH}^- \rightarrow \text{X}^- + \text{XO}^-$  in an aqueous medium, the rate of the reaction is given as

$$\frac{(d(\text{XO}^-))}{dt} = K \frac{[\text{X}^-][\text{XO}^-]}{[\text{OH}^-]}$$

The overall order for this reaction is

- |         |        |
|---------|--------|
| a. Zero | b. 1   |
| c. -1   | d. 1/2 |

### Comprehension 3

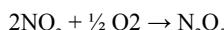
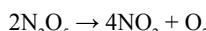
Arrhenius equation describes the effect of temperature on rate constant as  $0 K = Ae^{-E_a/RT}$

Here  $E_a$  represents activation energy,  $A$  represents frequency factor. The equation clearly indicates that an increase of temperature or lowering of  $E_a$  leads to increase in rate of reaction. According to collision theory steric factor ' $P$ ' is equally important and contributes to effective collisions. Now the modified form of Arrhenius equation is given as  $K = PZ_{AB} e^{-E_a/RT}$

- 158.** The activation energy for a simple chemical reaction  $X \rightarrow Y$  is  $E_a$  for forward direction. The value of  $E_a$  for backward direction may be

- a.  $-E_a$
- b.  $2E_a$
- c.  $>$  or  $< E_a$
- d. Zero

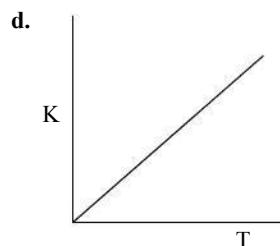
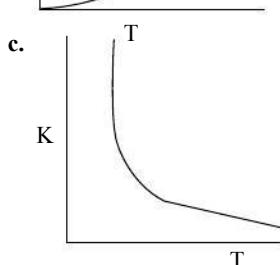
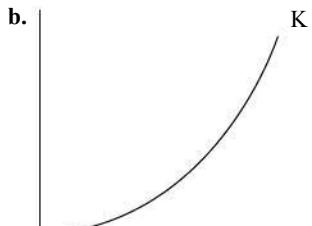
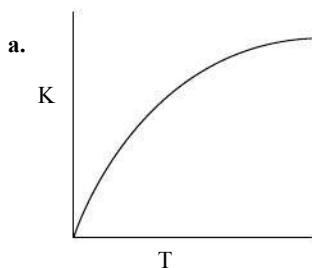
- 159.** For the following reaction at a particular temperature which takes place as follows



The value of activation energies are  $E_1$  and  $E_2$  respectively then

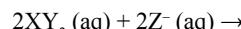
- a.  $E_1 > E_2$
- b.  $E_1 = 2E_2$
- c.  $2E_1 = E_2$
- d.  $E_1 < E_2$

- 160.** Which of the given graph represents the variation of rate constant ( $K$ ) verses temperature( $T$ )?

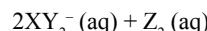


### Comprehension 4

In a hypothetical reaction given below



(Excess)



$XY_2$  oxidizes  $Z^-$  ion in aqueous solution to  $Z_2$  and gets reduced to  $XY_2^-$ .

The order of the reaction with respect to  $XY_2$  as concentration of  $Z^-$  is essentially constant.

$$\text{Rate} = k [XY_2]^m$$

Given below the time and concentration of  $XY_2$  taken

Time (s)	$(XY_2)$ M
0.00	$4.75 \times 10^{-4}$
1.00	$4.30 \times 10^{-4}$
2.00	$3.83 \times 10^{-4}$

- 161.** The order with respect to  $XY_2$  is

- a. 0
- b. 1
- c. 2
- d. 3

- 162.** The rate constant for this reaction is

- a. 0.02
- b. 0.01
- c. 0.2
- d. 0.1

- 163.** The half life of the reaction (in seconds) is

- a. 2.39
- b. 13.35
- c. 6.93
- d. 19.63

### Assertion-Reason Type Questions

In the following question two statements Assertion (A) and Reason (R) are given. Mark

- a. If A and R both are correct and R is the correct explanation of A;
- b. If A and R both are correct but R is not the correct explanation of A;
- c. A is true but R is false;

## 7.42 ■ Chemical Kinetics

- d. A is false but R is true,  
e. A and R both are false.
- 164.** (A): Order of reaction is an experimental property and irrespective of the fact whether the reaction is elementary or complicated, it is the sum of the powers of the concentration terms appearing in the rate law that is, experimentally observed rate law.  
(R): Order of reaction may change with change in experimental conditions.
- 165.** (A): Hydrolysis of methyl acetate in aqueous solution is a pseudo first order reaction.  
(R): In this reaction concentration of  $\text{H}_2\text{O}$  remains nearly constant during the course of the reaction.
- 166.** (A): A catalyst does not alter the heat of reaction.  
(R): Catalyst increases the rate of reaction.
- 167.** (A): In first order reaction  $t_{1/2}$  is independent of initial concentration.  
(R): The unit of K is  $\text{time}^{-1}$ .
- 168.** (A): If order with respect to species involved in any reaction is not equal to the stoichiometric coefficient of that species in the reaction then reaction must be an elementary reaction.  
(R): In an elementary reaction the order with respect to species involved is equal to the stoichiometric coefficients.
- 169.** (A): If temperature does not affect the rate of reaction,  $E_a = 0$   
(R): Lesser the activation energy, slower will be the reaction.
- 170.** (A): The rate constant increases exponentially with the increase in temperature.  
(R): With the rise in temperature, the average kinetic energy of the molecules increases.
- 171.** (A): Arrhenius equation explains the temperature dependence of rate of a chemical reaction.  
(R): Plots of  $\log K$  vs  $1/T$  are linear and the energy of activation is obtained from such plots.
- 172.** (A):  $2\text{FeCl}_3 + \text{SnCl}_2 \rightarrow \text{FeCl}_2 + \text{SnCl}_4$  is a 3<sup>rd</sup> order reaction  
(R): The rate constant for third order reaction has unit  $\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$ .
- 173.** (A):  $\text{NO}_2 + \text{CO} \rightarrow \text{CO}_2 + \text{NO}$   
 $\text{Rate} = k [\text{NO}_2]^2$   
The rate is independent of concentration of CO.  
(R): The rate does not depend upon [CO] because it is involved in fast step.
- 174.** (A): In order for molecules to interact, they must approach each other so closely to colloid with each other  
(R): Rearrangement of chemical bonds occur during collision. They must collide each other and rearrangement of chemical bonds occur during collision)
- 175.** (A): The rate of a reaction normally increases by a factor of 2 or 3 for every  $10^\circ\text{C}$  rise in temperature.  
(R): Increase in temperature increases the number of collisions.
- 176.** (A): A catalyst enhances the rate of reaction.  
(R): The energy of activation of the reaction is lowered in presence of a catalyst.
- 177.** (A): In rate laws, the exponents for concentration do not necessarily match the stoichiometric coefficients.  
(R): It is the mechanism and not the balanced chemical equation for the overall change that governs the reaction rate.
- 178.** (A): In rate laws, unlike in the expression for equilibrium constants, the exponents for concentrations do not necessarily match stoichiometric coefficients.  
(R): It is the mechanism and not the balanced chemical equation for the overall change the governs the reaction rate.  
Reaction rate is experimentally quantity and not necessary depends on stoichiometric coefficients
- 179.** (A): Order can be different from molecularity of a reaction.  
(R): Slow step is the rate determining step and may involve lesser number of reactants.
- 180.** (A): For the hydrogen halogen photochemical reaction, the quantum yield for the formation of HBr, is lower than that of HCl.  
(R):  $\text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H}$  has higher activation energy than  $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$

### Matrix-Match Type Questions

181. Match the following:

**List I**

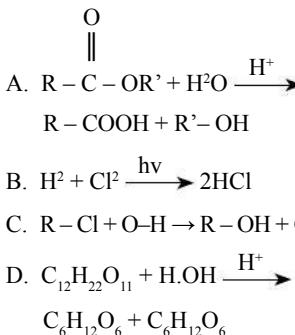
- A. Half life of zero order reaction
- B. Half life of first order reaction
- C. Temperature coefficient
- D. Half life of second order reaction

**List II**

- (p)  $a/2k$
- (q)  $0.693/k$
- (r)  $1/ka$
- (s)  $2 - 3$

182. Match the following:

**List I**



**List II**

- (p) Zero order
- (q) First order
- (r) Second order
- (s) Pseudo unimolecular

183. Match the following:

**List I**

- A. Temperature coefficient
- B. Order
- C. Ea for ionic reactants
- D. Radioactive disintegration

**List II**

- (p) Zero
- (q) Between 2 – 3
- (r) First
- (s)  $> 3$

184. Match the following:

**List I**

- 1. zero order reaction
- 2. first order reaction
- 3. second order reaction
- 4. third order reaction

**List II**

- (p)  $\text{mole}^{-1} \text{Lt sec}^{-1}$
- (q)  $\text{mole}^{-2} \text{Lt}^2 \text{sec}^{-1}$
- (r)  $\text{mole Lt}^{-1} \text{sec}^{-1}$
- (s)  $\text{sec}^{-1}$

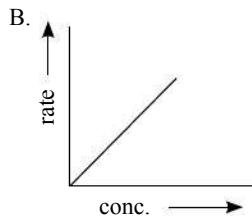
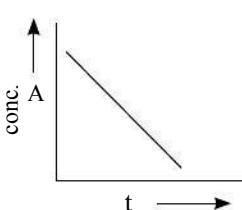
185. Match the following:

**List I**

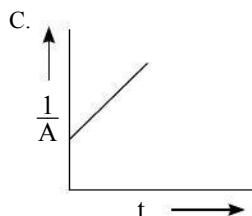
- A.

**List II**

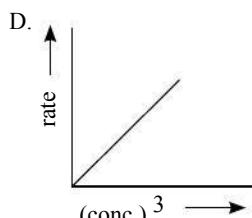
- (p) 1



(q) 2



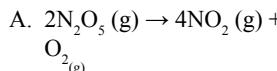
(r) 3



(s) 0

186. Match the following:

**List I (Reactions)**

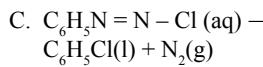
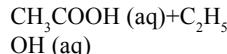


**List II**

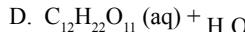
- (p) Titration of a liquid of reaction mixture with alkali



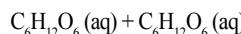
- (q) Measurement of pressure of reaction mixture at constant V and T



- (r) Measurement of optical activity



- (s) Measurement of volume of gas at constant P and T.



Glucose Fructose

187. Match the following:

(Here a = Initial concentration of the reactant,  
p = Initial pressure of the reactant)

## 7.44 ■ Chemical Kinetics

### List I

- A.  $t_{1/2} = \text{constant}$   
 B.  $t_{1/2} \propto a$   
 C.  $t_{1/2} \propto 1/a$   
 D.  $t_{1/2} \propto p^{-1}$

### List II

- (p) Zero order  
 (q) First order  
 (r) Second order  
 (s) Pseudo first order

188. Match the following:

### List I

- A.  $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$   
 B.  $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$   
 C.  $\text{C}_{12}\text{H}_{22}\text{O}_{11} (\text{aq}) + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 (\text{aq}) + \text{C}_6\text{H}_{12}\text{O}_6 (\text{aq})$   
 D.  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$

### List II

- (p) Zero order  
 (q) Ist order  
 (r) Pseudo Ist order  
 (s) Photo chemical reaction

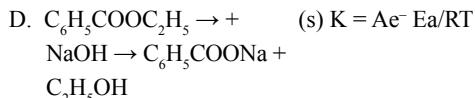
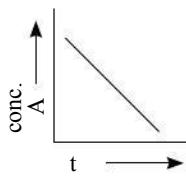
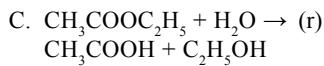
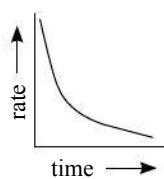
189. Match the following:

### List I

- A.  $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$   
 B.  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$

### List II

- (p)  $t_{1/2} = X \text{ min}$  as a constant temperature any time of the reaction.



190. Match the following:

For the reaction



If the graphs given in list I may be of these types

(i) Conc<sup>n</sup> vs time (x - axis)

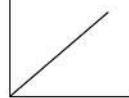
(ii)  $t^{1/2}$  vs Initial concn (a) (x- axis)

(iii) Rate ( $-dx$ ) vs time (x- axis)

(iv)  $\left(\frac{\text{Co} - \text{C}_t}{\text{C}_t}\right)^{\frac{1}{n}} \text{ vs time (x- axis)}$

### List I

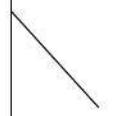
A.



### List II

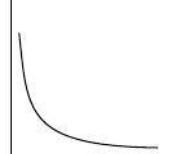
(p) Zero order

B.



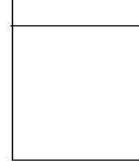
(q) Ist order

C.



(r) II<sup>nd</sup> order

D.



(s) Pseudo unimolecular

### The IIT-JEE Corner

191. The rate law has the form; Rate =  $k[A][B]^{3/2}$ , can the reaction be an elementary process?

- a. yes
- b. no
- c. may be yes or no
- d. can not be predicted

[IIT 1997]

192. The rate constant of a reaction is given by  $\ln k (\text{sec}^{-1}) = 14.34 - (1.25 \times 10^4) / T$

What will be the energy of activation?

- a. 24.83 kcal mol<sup>-1</sup>
- b. 49.66 kcal mol<sup>-1</sup>
- c. 12.42 kcal/mol
- d. none

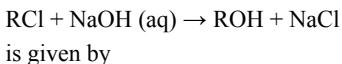
[IIT 1997]

193. For a first order reaction,

- a. The degree of dissociation is equal to  $(1 - e^{-kt})$   
 b. The pre-exponential factor in the Arrhenius equation has the dimensions of time  $T^{-1}$ .  
 c. The time taken for the completion of 75 % reaction is thrice the  $t \frac{1}{2}$  of the reaction.  
 d. both (a) and (b)

[IIT 1998]

194. The rate law for the reaction



Rate =  $k[\text{RCl}]$ . The rate of the reaction will be

- a. Doubled on doubling the concentration of sodium hydroxide  
 b. Halved on reducing the concentration of alkyl halide to one half  
 c. Decreased on increasing the temperature of reaction  
 d. Unaffected by increasing the temperature of the reaction.

[IIT 1998]

195. In the above equation, what is the value of Arrhenius factor?

- a.  $3 \times 10^6$       b.  $6.3 \times 10^9$   
 c.  $5.42 \times 10^{13}$       d.  $5.42 \times 10^{10}$

[IIT 1998]

196. The rate constant of a reaction is  $1.5 \times 10^7 \text{ s}^{-1}$  at  $50^\circ\text{C}$  and  $4.5 \times 10^7 \text{ s}^{-1}$  at  $100^\circ\text{C}$ . What is the value of activation energy?

- a.  $2.2 \times 10^3 \text{ J mol}^{-1}$   
 b.  $2300 \text{ J mol}^{-1}$   
 c.  $2.2 \times 10^4 \text{ J mol}^{-1}$   
 d.  $220 \text{ J mol}^{-1}$

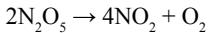
[IIT 1998]

197. The rate constant for an isomerization reaction  $\text{A} \rightarrow \text{B}$ , is  $4.5 \times 10^{-3} \text{ min}^{-1}$ . If the initial concentration of A is 1 M. Calculate the rate of reaction after 1 hour.

- a.  $0.34354 \text{ M min}^{-1}$   
 b.  $0.034354 \text{ M min}^{-1}$   
 c.  $0.0034354 \text{ M min}^{-1}$   
 d.  $0.0003454 \text{ M min}^{-1}$

[IIT 1999]

198. The rate constant for the reaction,



is  $3.0 \times 10^{-5} \text{ s}^{-1}$ . If the rate is  $2.40 \times 10^{-5} \text{ mol litre}^{-1} \text{ s}^{-1}$ , then the concentration of  $\text{N}_2\text{O}_5$  (in  $\text{mol litre}^{-1}$ ) is

- a. 1.4      b. 1.2  
 c. 0.04      d. 0.8

[IIT 2000]

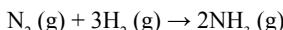
199. If 'I' is the intensity of absorbed light and 'C' is the concentration of AB for the photochemical process

$\text{AB} + \text{hv} \rightarrow \text{AB}^*$ , the rate of formation of  $\text{AB}^*$  is directly proportional to

- a. C      b. I  
 c.  $I^2$       d. C.I.

[IIT 2001]

200. Consider the chemical reaction,



The rate of this reaction can be expressed in terms of time derivatives of concentration of  $\text{N}_2 \text{ (g)}$ ,  $\text{H}_2 \text{ (g)}$  or  $\text{NH}_3 \text{ (g)}$ . Identify the correct relationship amongst the rate expressions.

- a. rate =  $-d[\text{N}_2]/dt = -1/3 d[\text{H}_2]/dt = \frac{1}{2} d[\text{NH}_3]/dt$   
 b. rate =  $-d[\text{N}_2]/dt = -3 d[\text{H}_2]/dt = 2 d[\text{NH}_3]/dt$   
 c. rate =  $-d[\text{N}_2]/dt = -1/3 d[\text{H}_2]/dt = 2d[\text{NH}_3]/dt$   
 d. rate =  $-d[\text{N}_2]/dt = d[\text{H}_2]/dt = d[\text{NH}_3]/dt$

[IIT 2002]

201. In a first order reaction the concentration of reactant decreases from  $800 \text{ mol/dm}^3$  to  $50 \text{ mol/dm}^3$  in  $2 \times 10^4 \text{ sec}$ . The rate constant of reaction in  $\text{sec}^{-1}$  is

- a.  $2 \times 10^4$       b.  $3.45 \times 10^{-5}$   
 c.  $1.386 \times 10^{-4}$       d.  $2 \times 10^{-4}$

[IIT 2003]

202. In a first order reaction the concentration of reactant decreases from  $800 \text{ mol/dm}^3$  to  $50 \text{ mol/dm}^3$  in  $2 \times 10^4 \text{ sec}$ . The rate constant of reaction in  $\text{sec}^{-1}$  is

- a.  $2 \times 10^4$       b.  $3.45 \times 10^{-5}$   
 c.  $1.386 \times 10^{-4}$       d.  $2 \times 10^{-4}$

[IIT 2003]

203. The reaction  $\text{X} \rightarrow \text{product}$  follows first order kinetics. In 40 minutes, the concentration of X changes from 0.1 M to 0.025 M, then the rate of reaction when concentration of X is 0.01 M is

- a.  $3.47 \times 10^{-5} \text{ M/min}$   
 b.  $1.73 \times 10^{-4} \text{ M/min}$   
 c.  $1.73 \times 10^{-5} \text{ M/min}$   
 d.  $3.47 \times 10^{-4} \text{ M/min}$

[IIT 2004]

204. Which of the following is incorrect about order of reaction?

- a. it is calculated experimentally  
 b. it is sum of powers of concentration in rate law expression

## 7.46 ■ Chemical Kinetics

- c. the order of reaction cannot be fractional
- d. there is not necessarily a connection between order and stoichiometry of a reaction.

[IIT 2005]

205. Consider a reaction  $aG + bH \rightarrow \text{Products}$ . When concentration of both the reactants G and H is doubled, the rate increases by eight times. However when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is

- a. 0
- b. 1
- c. 2
- d. 3

[IIT 2007]

206. For a first order reaction  $A \rightarrow P$ , the temperature (T) dependent rate constant ( $k$ ) was found to follow the equation

$\log k = -(2000) i/T + 6.0$ . The pre-exponential factor A and the activation energy  $E_a$ , respectively, are

- a.  $1.0 \times 10^6 \text{ s}^{-1}$  and  $9.2 \text{ kJ mol}^{-1}$
- b.  $6.0 \text{ s}^{-1}$  and  $16.6 \text{ kJ mol}^{-1}$
- c.  $1.0 \times 10^6 \text{ s}^{-1}$  and  $16.6 \text{ kJ mol}^{-1}$
- d.  $1.0 \times 10^6 \text{ s}^{-1}$  and  $38.3 \text{ kJ mol}^{-1}$

[IIT 2009]

## ANSWERS

### Straight Objective Type Questions

- |       |       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|-------|
| 1. c  | 2. b  | 3. a  | 4. b  | 5. c  | 6. b  | 7. c  | 8. c  |
| 9. b  | 10. d | 11. d | 12. d | 13. a | 14. a | 15. b | 16. c |
| 17. c | 18. b | 19. b | 20. d | 21. a | 22. c | 23. b | 24. a |
| 25. b | 26. a | 27. c | 28. b | 29. b | 30. c | 31. a | 32. b |
| 33. a | 34. d | 35. c | 36. b | 37. b | 38. d | 39. a | 40. b |
| 41. d | 42. b | 43. a | 44. d | 45. d | 46. d | 47. a | 48. b |
| 49. c | 50. d | 51. b | 52. c | 53. b | 54. a | 55. a | 56. d |
| 57. c | 58. b | 59. d | 60. a | 61. d | 62. a | 63. b | 64. c |
| 65. d | 66. a | 67. c | 68. b | 69. c | 70. d | 71. a | 72. c |
| 73. a | 74. a | 75. b | 76. d | 77. b | 78. c | 79. d | 80. c |

### Brainteasers Objective Type Questions

- |        |        |        |        |        |        |        |        |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 81. c  | 82. a  | 83. b  | 84. b  | 85. b  | 86. a  | 87. c  | 88. d  |
| 89. a  | 90. c  | 91. a  | 92. d  | 93. c  | 94. a  | 95. c  | 96. b  |
| 97. c  | 98. a  | 99. b  | 100. a | 101. b | 102. d | 103. c | 104. d |
| 105. a | 106. b | 107. c | 108. d | 109. d | 110. b | 111. b | 112. b |
| 113. c | 114. d | 115. a | 116. b | 117. c | 118. c | 119. a | 120. b |

### Multiple Correct Answer Type Questions

- |           |              |              |              |              |           |              |
|-----------|--------------|--------------|--------------|--------------|-----------|--------------|
| 121. a, b | 122. a, d    | 123. a, b, d | 124. c, d    | 125. b, c    | 126. c, d | 127. b, c, d |
| 128. a, d | 129. a, b, d | 130. b, d    | 131. a, c    | 132. a, b, c | 133. b, d | 134. a, b, d |
| 135. b, d | 136. b, c    | 137. b, d    | 138. a, b    | 139. b, c    | 140. a, d | 141. b, c, d |
| 142. a, d | 143. a, b    | 144. c, d    | 145. b, c, d | 146. a, b    | 147. b, d | 148. b, c, d |
| 149. a, b | 150. c, d    |              |              |              |           |              |

### Matrix-Match Type Questions

- |                                                 |                                              |
|-------------------------------------------------|----------------------------------------------|
| 181. a-(p), b-(q), c-(s), d-(r)                 | 182. a-(q,s), b-(p), c-(r), d-(q, s)         |
| 183. a-(q), b-(p, r, s), c-(p), d-(r)           | 184. a-(r), b-(s), c-(p), d-(q)              |
| 185. a-(s), b-(p), c-(q), d-(r)                 | 186. a-(q), b-(p), c-(s), d-(r)              |
| 187. a-(q, s), b-(p), c-(p, r), d-(p, r)        | 188. a (q), b (p, s) , c (q, r) d (p)        |
| 189. a (r), b (p, q, s), c (p, q, s ), d (p, q) | 190. a (p, r), b (p , c (q, s) , d (p, q, s) |

### Assertion Reason Type Questions

- |        |        |        |        |        |        |        |        |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 164. b | 165. a | 166. b | 167. a | 168. d | 169. c | 170. b | 171. b |
| 172. b | 173. a | 174. a | 175. b | 176. a | 177. a | 178. a | 179. a |
|        |        |        |        |        |        |        | 180. a |

### Linked-Comprehension Type Questions

#### Comprehension 1

151. b      152. c      153. b

#### Comprehension 2

154. b      155. b      156. A      157. A

#### Comprehension 3

158. c      159. b      160. b

#### Comprehension 4

161. b      162. d      163. c

#### The IIT-JEE Corner

- |        |        |        |        |
|--------|--------|--------|--------|
| 191. b | 192. a | 193. d | 194. b |
| 195. d | 196. c | 197. c | 198. d |
| 199. b | 200. a | 201. c | 202. c |
| 203. d | 204. c | 205. d | 206. d |

### Hints and Explanations

- It is a characteristics constant of a particular reaction at a given temperature. It does not depend upon initial concentration of the reactants, time of reaction and extent of reaction.
- k depends upon temperature.
- $\text{Rate} = -\frac{1}{3} \frac{d(A)}{dt} = \frac{1}{2} \frac{d(B)}{dt}$   
 $= -\frac{2}{3} \frac{d(A)}{dt}$
- Catalyst lowers the activation energy barrier and thus it shortens the time to reach equilibrium.
- Order  $= \frac{1}{2} + \frac{1}{3} + \frac{1}{4} = \frac{6+4+3}{12}$   
 $= 13/12$
- From the units of rate constant ( $10^{-3} \text{ min}^{-1}$ ) it is found that it is a first order reaction.

$$\begin{aligned} r &= k [\text{conc.}] \\ &= 10^{-3} \times 0.2 \\ &= 0.0002 \text{ mol dm}^{-3} \text{ min}^{-1} \end{aligned}$$

- For an endothermic reaction,  $E_a$  will be more than  $\Delta H$  while for an exothermic reaction,  $E_a$  will be less than  $\Delta H$ .
- When the volume is reduced to  $\frac{1}{4}$  th, concentration becomes four times. Since it is a second order reaction, so rate become 16 times.
- $k = Ae^{-E_a/RT}$  (Arrhenius equation)  
when  $T \rightarrow \infty$   
 $k = A e^0$ , or  $k = A$   
Thus  $k = 6 \times 10^{14} \text{ s}^{-1}$
- $r = k [A] = 60 \times 10^{-4} \times 0.01$

## 7.48 ■ Chemical Kinetics

$$= 60 \times 10^{-4} \times \frac{1}{10^2}$$

$$= 60 \times 10^{-6} \text{ mol l}^{-1} \text{ min}^{-1}$$

22. The rate of reaction is given as

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

25. Rate =  $k [N_2O_5]^1$

$$[N_2O_5]^1 = \text{Rate}/k$$

$$= \frac{1.02 \times 10^{-4}}{3.4 \times 10^{-5}} = 3$$

29. For a first order kinetics,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$\text{At } t_{1/2}, k = \frac{2.303}{t_{1/2}} \log_{10} \frac{a}{a-a/2}$$

$$t_{1/2} = \frac{2.303}{k} \log_{10} 2 = \frac{\ln 2}{k}$$

84. From expt 2 and 3 it is clear that when (A) is doubled keeping (B) constant, rate becomes four times, thus  $r \propto [A]^2$

Now rate equation is  $r = k [A]^2 [B]^n$ .

From expt. 1 and 2

$$5 \times 10^{-4} = k [2.5 \times 10^{-4}]^2 [3 \times 10^{-5}]^n \quad \dots \dots \dots (1)$$

$$4 \times 10^{-3} = k [5 \times 10^{-4}]^2 [6 \times 10^{-5}]^n \quad \dots \dots \dots (2)$$

divide 2 and 1

$$\frac{4 \times 10^{-3}}{5 \times 10^{-4}} = \frac{k [5 \times 10^{-4}]^2 [6 \times 10^{-5}]^n}{k [2.5 \times 10^{-4}]^2 [3 \times 10^{-5}]^n}$$

$$8 = 2^2 \cdot 2^n$$

$$2^n = 8/4 = 2^1$$

$$n = 1$$

$$r = k [A]^2 [B]^1$$

89. At 450°C,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10.17 \text{ min}}$$

$$= 0.0681 \text{ min}^{-1}$$

Now for 75 % decomposition

$$x = 75 \% \text{ of } a = 0.75 a$$

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

$$= \frac{2.303}{0.0681 \text{ min}^{-1}} \log \frac{a}{a-0.75a}$$

$$= \frac{2.303}{0.0681 \text{ min}^{-1}} \log \frac{1}{0.25}$$

$$= 20.39 \text{ min}$$

92. Rate =  $k[A]$  (It is a first order reaction)

$$k = \frac{r}{[A]} = \frac{2.0 \times 10^{-5} \text{ Ms}^{-1}}{0.01 \text{ M}}$$

$$= \frac{2 \times 10^{-5} \text{ s}^{-1}}{10^{-2}} = 2 \times 10^{-3} \text{ s}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2 \times 10^{-3} \text{ s}}$$

$$= 346.5 \text{ s} = 347 \text{ s}$$

94. As it is the slowest step so it is rate determining step.

$$r = K [H_2(g)] [ICl(g)]$$

96. For a first order reaction,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$k = \frac{2.303}{60} \log_{10} \frac{100}{40} = \frac{2.303}{60} \times \log_{10} 2.5$$

$$= 0.0153$$

$$t_{1/2} = \frac{2.303}{k} \log_{10} \frac{100}{50} = \frac{2.303}{0.0153} \times \log_{10} 2$$

$$= 45.31 \text{ min.}$$

101. The order of an elementary reaction is determined experimentally and therefore statement two is not correct.

105. Pseudo unimolecular reactions are in presence of one or more reactants in excess. Usually such reactions are conducted in solvents, which are themselves one of the reactants.

107. Statement (1) is not correct because sum of powers raised to concentration terms in the rate law denotes the order of reaction, which is  $1 + 1 = 2$  and not equal to unity.

108. The stoichiometric coefficients of reaction has no relation to the order of reaction.

110. According to the rate law

$$\text{Rate} = k [A] [B]$$

From first experiment we have

$$2 \times 10^{-4} = k (1 \times 10^{-2}) (2 \times 10^{-2})$$

$$k = 2$$

The rate law: Rate =  $k [A][B]$  shows that rate of reaction becomes four times the original rate, when the concentration of each reactant is doubled.

113. As mol L<sup>-1</sup> of  $N_2O_5$  reacted =  $2 \times 0.1 = 0.2$

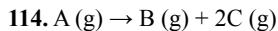
$$\text{So } [N_2O_5] \text{ left} = 1.0 - 0.2 = 0.8 \text{ mol L}^{-1}$$

$$\text{Rate of reaction} = k \times [N_2O_5]$$

$$= 3.0 \times 10^{-4} \times 0.8 = 2.4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{Rate of formation of } NO_2 = 4 \times 2.4 \times 10^{-4}$$

$$= 9.6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$



At 320 seconds,  $x$  moles of A decomposes giving  $x$  moles of B and  $2x$  moles of C.

$$\text{Total number of moles} = a - x + x + 2x \\ = a + 2x$$

So number of moles has increased by  $2x$ .

$$2x = 96 \text{ mm}$$

$$x = 48 \text{ mm.}$$

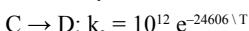
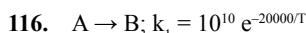
For a first order reaction,

$$5.2 \times 10^{-4} = \frac{2.303}{320} \log_{10} \frac{a}{a - 48} .$$

$$\text{Solving, } \log \frac{a}{a - 48} = 0.07225$$

Solving,

$$a = 313 \text{ mm.}$$



$$\text{When } k_1 = k_2$$

$$10^{10} e^{-20000/T} = 10^{12} e^{-24606/T}$$

$$e^{-4606/T} = 100$$

$$\frac{4606}{T} = 2.303 \log 100$$

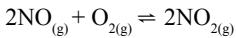
$$\frac{4606}{T} = 2.303 \times 2$$

$$\text{As, } T = \frac{4606}{2.303 \times 2} = 1000 \text{ K}$$

117. According to the given data, when concentration of  $\text{Br}_2$  is doubled, the initial rate of disappearance of  $\text{Br}_2$  remains unaffected. So order of reaction with respect to  $\text{Br}_2$  is zero. The rate law for the reaction will be:

$$k[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

118. For a given reaction –



$$\text{Rate of reaction} = k [\text{NO}]^2 [\text{O}_2]$$

Rate of reaction directly proportional to concentration of the compound or inversely proportional to the volume of the vessel.

$$\text{that is, } C \propto \frac{n}{V}$$

If volume of vessel is reduced by 1/3rd of its initial value, then concentration of compound is increased by 3 times and consequently the rate of reaction by 27 times.

119. When the reactants are A, B and C at one mole per litre each the rate equation is, rate =  $k [A]^X [B]^{1/Y} [C]^{X/Y}$ . The order of the reaction is

$$(A) X + \frac{(1+X)}{Y}$$

$$(B) X - Y + \frac{X}{Y}$$

$$(C) X + Y + \frac{X}{Y}$$

$$(D) 2(X + Y)$$

$$\text{rate} = k [A]^X [B]^{1/Y} [C]^{X/Y}$$

$$\text{order} = X + \frac{1}{Y} + \frac{X}{Y}$$

$$= X + \frac{(1+X)}{Y}$$

120.  $\frac{[C]}{[A][B]} = \frac{k_1}{k_2}$  (equilibrium constant)

$$\text{So } [C] = \frac{k_1 [A][B]}{k_2} \quad \dots \dots (1)$$

$$\frac{d[D]}{dt} = k_3 [C] \quad \dots \dots (2)$$

From (1) and (2)

$$\frac{d[D]}{dt} = \frac{k_3 \cdot k_1}{k_2} [A][B]$$

174. They must collide each other and rearrangement of chemical bonds occur during collision.

178. Reaction rate is experimentally quantity and not necessarily depends on stoichiometric coefficients.

192. Compare with the equation

$$\ln k = \ln A - \frac{Ea}{RT}$$

$$\text{Thus, } \frac{Ea}{R} = 1.25 \times 10^4$$

$$\text{and } Ea = R \times 1.25 \times 10^4$$

$$Ea = \frac{1.98}{1000} \times 1.25 \times 10^4$$

$$Ea = 24.75 \text{ Kcal mol}^{-1}$$

194. It is a pseudo first order reaction. Since  $r \propto (RCI)$ , so rate is halved when the conc. of alkyl halide is halved.

195.  $\log k = \log A - \frac{Ea}{2.303 RT}$

$$\log 1.5 \times 10^7 = \log A - \frac{22011}{2.303 \times 8.314}$$

$$7 + \log 1.5 = \log A - 3.5591$$

$$\log A - \log 1.5 = 10.5591$$

$$\log \frac{A}{1.5 \text{ s}^{-1}} = 10.5591$$

$$A = \text{Antilog}(10.5591) = 3.615 \times 10^{10}$$

$$1.5 \text{ s}^{-1}$$

$$\text{Now, } A = 3.615 \times 10^{10} \times 1.5 \\ = 5.4225 \times 10^{10} \text{ s}^{-1}$$

## 7.50 ■ Chemical Kinetics

196.  $k_1 = 1.5 \times 10^7 \text{ s}^{-1}$ ,  $k_2 = 4.5 \times 10^7 \text{ s}^{-1}$

$$T_1 = 50 + 273 = 323 \text{ K},$$

$$T_2 = 100 + 273 = 373 \text{ K}$$

$$\log \frac{k_2}{k_1} = \frac{Ea}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log \frac{4.5 \times 10^7}{1.5 \times 10^7} = \frac{Ea}{2.303 \times 8.31}$$

$$\left( 4 \frac{373 - 323}{373 \times 323} \right)$$

$$\log 3 = \frac{Ea \times 50}{19.147 \times 373 \times 323}$$

$$\text{or } 0.4771 = \frac{Ea \times 50}{19.147 \times 373 \times 323}$$

on solving,  $Ea = 22.11 \text{ J/mole}$

$\approx 2.2 \times 10^4 \text{ J/mole}$

197.  $a = 1 \text{ M}$ ,  $t = 60 \text{ min}$ ,  $k = 4.5 \times 10^{-3} \text{ min}^{-1}$

$$a - x = ?$$

$$k = \frac{2.303}{t} \log \frac{a}{a-x} .$$

$$\log \frac{a}{a-x} = \frac{kt}{2.303} = \frac{4.5 \times 10^{-3} \times 60}{2.303}$$

$$\text{or } \log \frac{a}{a-x} = 0.1172$$

$$\frac{a}{a-x} = \text{Antilog}(0.1172) = 1.31$$

$$\frac{1}{a-x} = 1.31$$

$$a - x = \frac{1}{1.31} = 0.7633$$

After one hour, conc. of A is  $(a - x) = 0.7633$

Rate of reaction after 1 hour =  $k$  (conc.)

$$= 4.5 \times 10^{-3} \times 0.7633$$

$$= 3.43 \times 10^{-3} \text{ M min}^{-1}$$

198.  $r = k [N_2O_5]^1$

$$[N_2O_5] = \frac{r}{k} = \frac{2.40 \times 10^{-5}}{3 \times 10^{-5}} = 0.8$$

199. The rate of formation of  $AB^*$  is directly proportional to the intensity of incident light ( $I$ ).

200. Rate =  $-\frac{d[N_2]}{dt} = -\frac{1}{3} \frac{d[H_2]}{dt}$

$$= + \frac{1}{2} \frac{d[NH_3]}{dt}$$

201.  $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$

$$= \frac{2.303}{2 \times 10^4 \text{ s}^{-1}} \log \frac{800}{50}$$

$$= 1.386 \times 10^{-4} \text{ s}^{-1}.$$

202.  $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$

$$= \frac{2.303}{2 \times 10^4 \text{ s}^{-1}} \log \frac{800}{50}$$

$$= 1.386 \times 10^{-4} \text{ s}^{-1}.$$

203.  $k = \frac{2.303}{t} \log \frac{C_0}{C_t} = \frac{2.303}{40 \text{ min}}$

$$\log \frac{0.1 \text{ M}}{0.025 \text{ M}} .$$

$$= \frac{2.303}{40} \log 4 = \frac{2.303 \times 0.6021}{40} \text{ min}^{-1}$$

$$\text{Rate} = k[A] = \frac{2.303 \times 0.6021}{40} \text{ min}^{-1}$$

$$\times 0.01 \text{ M}$$

$$= 3.47 \times 10^{-4} \text{ M/min}$$

205.  $aG + bH \rightarrow \text{Product}$

$$\text{rate} \propto [G]^a [H]^b$$

$$a = 1, b = 2$$

The overall order of reaction =  $1 + 2 = 3$

206. Here

$$\log K = 6 - \frac{2000}{T}$$

$$\text{As, } \log K = \frac{\log A - Ea}{2303 RT}$$

$$\text{So, } A = 10^6 \text{ sec}^{-1} \text{ and } Ea = 38.3 \text{ kJ/m}$$

## Numericals For Practice

1. In a first order reaction, the concentration of the reactant, decreases from  $0.8 \text{ M}$  to  $0.4 \text{ M}$  in  $15 \text{ minutes}$ . The time taken for the concentration to change from  $0.1 \text{ M}$  to  $0.025 \text{ M}$  is

a. 30 minutes

b. 60 minutes

c. 7.5 minutes

d. 15 minutes

2. For the reaction  $aA \rightarrow xP$  when  $[A] = 2.2 \text{ mM}$  the rate was found to be  $2.4 \text{ mM s}^{-1}$ . On reducing concentration of A to half, the rate changes to  $0.6 \text{ mM s}^{-1}$ . The order of reaction with respect to A is

a. 1.5

b. 2.0

c. 2.5

d. 3.0

3. The following data are obtained from the decomposition of a gaseous compound

Initial pressure , atm	1.6	0.8	0.4
Time for 50% reac., min	80	113	160

The order of the reaction is

- a. 0.5
- b. 1.0
- c. 1.5
- d. 2.0

4. What will be initial rate of a reaction if its constant is  $10^{-3} \text{ min}^{-1}$  and the concentration of reactant is 0.2 mol dm $^{-3}$ ?

- a. 0.02 mol dm $^{-3}$  min $^{-1}$
- b. 0.002 mol dm $^{-3}$  min $^{-1}$
- c. 0.0002 mol dm $^{-3}$  min $^{-1}$
- d. 2 mol dm $^{-3}$  min $^{-1}$

5. In a zero order reaction, 47.5% of the reactant remains at the end of 2.5 hours. The amount of reactant consumed in one hour is

- a. 10.5 %
- b. 32.0 %
- c. 52.6 %
- d. 21.0 %

6. The data given below is for the reaction of NO and Cl<sub>2</sub> to form NOCl at 295 K

[Cl <sub>2</sub> ]	[NO]	Initial rate (mol l $^{-1}$ s $^{-1}$ )
0.05	0.05	$1 \times 10^{-3}$
0.15	0.05	$3 \times 10^{-3}$
0.05	0.15	$9 \times 10^{-3}$

What is the rate law?

- a.  $r = k [NO] [Cl_2]$
- b.  $r = k [Cl_2]^1 [NO]^2$
- c.  $r = k [Cl_2]^2 [NO]$
- d.  $r = k [Cl_2]^1$

7. A gaseous compound decomposes on heating as per the following equation:

A(g)  $\rightarrow$  B (g) + 2C (g). After 5 minutes and 20 seconds, the pressure increases by 96 mm Hg. If the rate constant for this first order reaction is  $5.2 \times 10^{-4} \text{ s}^{-1}$ , the initial pressure of A is

- a. 480 mm
- b. 376 mm
- c. 696 mm
- d. 313 mm

8. For a reaction, A  $\rightarrow$  B + C, it was found that at the end of 10 minutes from the start. The total optical rotation of the system was 50° and when the reaction is complete it was 100°. Assume that only B and C are optically active and dextro rotatory, the rate constant of this first order reaction would be

- a.  $6.9 \text{ min}^{-1}$
- b.  $0.069 \text{ min}^{-1}$
- c.  $0.69 \text{ min}^{-1}$
- d.  $6.9 \times 10^{-2} \text{ min}^{-1}$

9. For the elementary reaction,  $2\text{NO} + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$ , the half life time is 19.2 sec at 820°C when partial pressure of NO and H<sub>2</sub> are 60 mm of Hg and 10 mm of Hg respectively. The value of half-life time at the same temperature when partial pressure of NO and H<sub>2</sub> are 600 mm of Hg and 20 mm of Hg respectively would be

- a. 10.9 sec
- b. 19.2 sec
- c. 119 sec
- d. 90.2 sec

10. At 380°C, half life period for the first order decomposition of H<sub>2</sub>O<sub>2</sub> is 360 min. The energy of activation of the reaction is 200 kJ mol $^{-1}$ . Calculate the time required for 75 % decomposition at 450°C if half life for decomposition of H<sub>2</sub>O<sub>2</sub> is 10.17 min at 450°C.

- a. 20.4 min
- b. 408 min
- c. 10.2 min
- d. none

11. Two reactions one of first order and other of second order have same values of rate constants ( $k_1' = k_2'$ ) when concentrations are expressed in mole dm $^{-3}$ . If the concentrations are expressed in mole ml $^{-1}$  the relation between their rate constant k<sub>1'</sub> and k<sub>2'</sub> will be

- a.  $k_1' = 10 k_2'$
- b.  $k_1' = k_2'$
- c.  $k_1' \times 10^3 = k_2'$
- d.  $k_2' \times 10^3 = k_1'$

12. The rate constant of a first order reaction, A  $\rightarrow$  products, is  $60 \times 10^{-4} \text{ s}^{-1}$ . Its rate at  $[A] = 0.01 \text{ mol l}^{-1}$  would be

- a.  $60 \times 10^{-6} \text{ mol l}^{-1} \text{ min}^{-1}$
- b.  $36 \times 10^{-4} \text{ mol l}^{-1} \text{ min}^{-1}$
- c.  $60 \times 10^{-2} \text{ mol l}^{-1} \text{ min}^{-1}$
- d.  $36 \times 10^{-1} \text{ mol l}^{-1} \text{ min}^{-1}$

13. At a given instant there are 25 % undecayed radioactive nuclei in a sample. After 10 seconds the number of undecayed nuclei reduces to 12.5%. The time in which the number of undecayed nuclei will further reduce to 6.25 % of the reduced number is

- a. 20 sec
- b. 40 sec
- c. 30 sec
- d. 10 sec

14. The activation energies of two reactions are 18 kJ mol $^{-1}$  and 4.0 kJ mol $^{-1}$  respectively. Assuming the pre-exponential factor to be the same for both reactions, the ratio of their rate constants at 27°C is

- a.  $3.66 \times 10^{-3}$
- b.  $3.612 \times 10^{-10}$
- c.  $6.312 \times 10^{-8}$
- d.  $3.612 \times 10^{-8}$

15. The activation energy of a reaction is zero. The rate constant (k) of the reaction at 280 K of the reaction at 280 K is  $1.6 \times 10^{-6} \text{ s}^{-1}$ . The value of the velocity constant for this reaction at 300 K is

- a. Zero
- b.  $1.6 \times 10^{-6} \text{ s}^{-1}$
- c.  $3.2 \times 10^{-6} \text{ s}^{-1}$
- d.  $1.6 \times 10^{-5} \text{ s}^{-1}$

## 7.52 ■ Chemical Kinetics

16. From the following data for the reaction between A and B

[A] mol l <sup>-1</sup>	[B] mol l <sup>-1</sup>	initial rate 300 K	(mol l <sup>-1</sup> s <sup>-1</sup> ) 320 K
$2.5 \times 10^{-4}$	$3.0 \times 10^{-5}$	$5.0 \times 10^{-4}$	$2.0 \times 10^{-3}$
$5.0 \times 10^{-4}$	$6.0 \times 10^{-5}$	$4.0 \times 10^{-3}$	—
$1.0 \times 10^{-3}$	$6.0 \times 10^{-5}$	$1.6 \times 10^{-2}$	—

Calculate the rate equation.

- a.  $r = k [B]^1$       b.  $r = k [A]^2$   
 c.  $r = k [A]^2 [B]^1$       d.  $r = k [A] [B]$

17. For the reaction,  $C_2H_4 + H_2 \rightarrow C_2H_6$ ,  $\Delta E^\circ = -30$  kcal. If the reaction is reversible and if the activation energy for the forward reaction is 28.0 kcal and its drops to 10.5 kcal in the presence of a catalyst, the activation energies for the uncatalysed and catalysed reverse reaction are respectively (in kcal)
- a. 58, 40.5      b. -58, -40.5  
 c. 40.5, 58      d. 58.0, -58.0

18. For the thermal rearrangement of vinyl allyl ether  $= 5 \times 10^{11} \exp(-128000/RT)$ , where k is in  $s^{-1}$  and activation energy in  $J \text{ mol}^{-1}$ . The enthalpy of activation in  $\text{kJ mol}^{-1}$  is
- a. 224.3      b. 142.3  
 c. 12.43      d. 124.3

19. The decomposition of  $N_2O_5$  in chloroform was followed by measuring the volume of  $O_2$  gas evolved:  $2N_2O_5 \rightarrow 2N_2O_4 + O_2$  (g). The maximum volume of  $O_2$  gas obtainable was  $100 \text{ cm}^3$ . In 500 minutes,  $90 \text{ cm}^3$  of  $O_2$  were evolved. The first order rate constant of the reaction, in  $\text{min}^{-1}$ , is

- a.  $\frac{100}{10 \times 500}$       b.  $\frac{2.303}{500} \log \frac{90}{100}$ .  
 c.  $\frac{2.303}{500}$       d.  $\frac{2.303}{500} \log \frac{100}{90}$

20. For the reaction  $Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$ , the initial concentration of  $I^-$  was  $0.20 \text{ mol lit}^{-1}$  and the concentration after 20 min was  $0.18 \text{ mol lit}^{-1}$ . Then the rate of formation of  $I_2$  in  $\text{mol lit}^{-1} \text{ min}^{-1}$  would be
- a.  $5 \times 10^{-4}$       b.  $2 \times 10^{-3}$   
 c.  $5 \times 10^{-3}$       d.  $1 \times 10^{-3}$

21. The rate of the reaction  $A + 2B \rightarrow 3C$  gets increased by 72 times when the concentration of A is tripled and that of B is doubled. The order of the reaction with respect to A and B are ..... and ..... respectively
- a. 2, 2      b. 1, 2  
 c. 2, 3      d. 3, 2

22. The isomerization of cyclopropane to propene is of first order with  $k = 8.25 \times 10^{-4} \text{ s}^{-1}$  at  $500^\circ\text{C}$ . If cyclopropane is enclosed in a heated tube at  $500^\circ\text{C}$ , the minimum time needed to yield at least 10% propene in resultant gas sample will be

- a. 172.4 s      b. 270.2 s  
 c. 127.7 s      d. 321.5 s

23. Radium has atomic weight 226 and half life of 1600 years. The number of disintegration produced per second from one gram are:

- a.  $1.7 \times 10^9$       b.  $3.6 \times 10^8$   
 c.  $3.7 \times 10^{10}$       d.  $4.6 \times 10^{10}$

24. If 60% of a first order reaction was completed in 60 minutes, 50 % of the same reaction would be completed in approximately

- a. 50 minutes      b. 45 minutes  
 c. 60 minutes      d. 40 minutes  
 $(\log 4 = 0.60, \log 5 = 0.69)$

25. The activation energy of a reaction is 94.14 kJ/mole and the value of rate constant at  $313 \text{ K}$  is  $1.8 \times 10^{-5} \text{ s}^{-1}$ . Calculate frequency factor A.

(Given  $E_a/2.303 RT = 15.7082, \log_{10} 18 = 0.2553$ )

- a.  $9.19 \times 10^{10}$  collision/sec  
 b.  $91.9 \times 10^{10}$  collision/sec  
 c.  $198.5 \times 10^{11}$  collision/sec  
 d.  $1.984 \times 10^{10}$  collision /sec

26. On introducing a catalyst at  $500 \text{ K}$ , the rate of a first order reaction increases by 1.718 times. The activation energy in presence of a catalyst is 4.15  $\text{kJ mol}^{-1}$ . The slope of the plot of  $\ln k$  (in  $\text{sec}^{-1}$ ) vs  $1/T$  ( $T$  is in K) in the absence of the catalyst is

- a. -1000      b. -100  
 c. +100      d. -10

27. One mole of  $N_2O_4$  gas at  $300 \text{ K}$  is kept in a closed container at 1 atm. It is heated to  $600 \text{ K}$  when 20 % by mass of  $N_2O_4$  decomposes to  $NO_2$  (g). The resultant pressure in the container would be

- a. 1.0 atm      b. 1.2 atm  
 c. 2.4 atm      d. 2.0 atm

28. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at  $25^\circ\text{C}$  are  $3.0 \times 10^{-4} \text{ s}^{-1}$ ,  $104.4 \text{ kJ mol}^{-1}$  and  $6 \times 10^{14} \text{ s}^{-1}$  respectively. The value of the rate constant as  $T \rightarrow \infty$  is

- a.  $2.0 \times 10^{18} \text{ s}^{-1}$       b.  $6.0 \times 10^{14} \text{ s}^{-1}$   
 c. infinity      d.  $3.6 \times 10^{30} \text{ s}^{-1}$

29. The rate of a certain hypothetical reaction  $A + B + C \rightarrow \text{Products}$  is given by

$$r = -\frac{d[A]}{dt} = k [A]^{1/2} [B]^{1/3} [C]^{1/4}$$

The order of the reaction is

- a. 13/12                  b. 13/14  
 c. 12/13                  d. 13/11

30. A reaction  $P \rightarrow Q$  is completed 25% in 25 min, 50 % completed in 25 min if  $[P]$  is halved, 25 % completed in 50 min if  $[P]$  is doubled. The order of reaction is

- a. Zero                  b. 1  
 c. 2                  d. 3

ANSWER KEYS	Q.	Ans.								
	1.	a	2.	b	3.	c	4.	c	5.	d
	6.	b	7.	d	8.	b	9.	b	10.	a
	11.	d	12.	a	13.	b	14.	a	15.	b
	16.	c	17.	a	18.	d	19.	c	20.	a
	21.	c	22.	c	23.	c	24.	b	25.	b
	26.	a	27.	c	28.	b	29.	b	30.	a

## Hints and Explanations

### 1. Order 1

Concentration changes from 0.8 M to 0.4 M in (50 %) 15 minutes this half life is = 15 minutes =  $T_{50}$

A change from 0.1 M to 0.025 M is 75 % and for first order reaction

$$T_{75} = 2 \times T_{50} = 2 \times 15 = 30 \text{ minutes}$$

$$T_{50} = 15 \text{ minutes}$$

$$k = \frac{2.303 \log 2}{T_{50}} = \frac{2.303 \log 2}{15}$$

$$\alpha = 0.1 \text{ M}$$

$$(\alpha - x) = 0.025 \text{ M}$$

for first order :

$$k = \frac{2.303}{t} \log \left( \frac{\alpha}{\alpha - x} \right)$$

$$\frac{2.303 \log 2}{15} = \frac{2.303}{t} \log \frac{0.1}{0.025}$$

$$= \frac{2.303}{t} \log 4$$

$$\frac{2.303 \log 2}{15} = \frac{2 \times 2.303 \log 2}{t}$$

$$t = 30 \text{ minutes.}$$

### 2. $aA \rightarrow xP$

$$\text{Rate of reaction} = [A]^a$$

$$\text{Order of reaction} = a.$$

$$[A]_1 = 2.2 \text{ mM}, r_1 = 2.4 \text{ mM s}^{-1} \quad \dots \dots \text{(i)}$$

$$[A]_2 = \frac{2.2}{2} \text{ mM}, r_2 = 0.6 \text{ mM s}^{-1} \text{ or } \frac{2.4}{4}$$

on reducing the concentration of A to half, the rate of reaction is decreased by four times.

$$\text{Rate of reaction} = [A]^2$$

$$\text{Order of reaction} = 2$$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{80}{113} = (p_2/p_1)^{n-1}$$

Here  $p_2, p_1$  are the initial pressures

$$80/113 = (0.8/1.6)^{n-1}$$

Taking logarithms,

## 7.54 ■ Chemical Kinetics

$$\log 0.7 = (n - 1) \log 0.5$$

on solving,

$$n = 1.5$$

4. From the units of rate constant ( $10^{-3} \text{ min}^{-1}$ ) it is found that it is a first order reaction.

$$r = k [\text{conc.}]$$

$$= 10^{-3} \times 0.2$$

$$= 0.0002 \text{ mol dm}^{-3} \text{ min}^{-1}$$

5. In a zero order reaction, the rate remains constant.

$$\text{Rate of reaction, } -\frac{d[c]}{dt} = \frac{52.5}{2.5}$$

$$= 21 \text{ moles lit}^{-1} \text{ hour}^{-1}$$

In our hour, the amount of reactant consumed = 21 %.

6. From expt 2 and 3 it is clear that when (A) is doubled keeping (B) constant, rate becomes four times, thus  $r \propto [A]^2$

Now rate equation is  $r = k [A]^2 [B]^n$

From expt. 1 and 2

$$5 \times 10^{-4} = k [2.5 \times 10^{-4}]^2 [3 \times 10^{-5}]^n \quad \dots \dots \dots (1)$$

$$4 \times 10^{-3} = k [5 \times 10^{-4}]^2 [6 \times 10^{-5}]^n \quad \dots \dots \dots (2)$$

divide 2 and 1

$$\frac{4 \times 10^{-3}}{5 \times 10^{-4}} = \frac{k [5 \times 10^{-4}]^2 [6 \times 10^{-5}]^n}{k [2.5 \times 10^{-4}]^2 [3 \times 10^{-5}]^n}$$

$$8 = 2^2 \cdot 2^n$$

$$2^n = 8/4 = 2^{10}$$

$$n = 1$$

$$r = k [A]^2 [B]^1$$

7.  $A(g) \rightarrow B(g) + 2C(g)$

At 320 seconds, x moles of A decomposes giving x moles of B and 2x moles of C.

$$\text{Total number of moles} = a - x + x + 2x$$

$$= a + 2x$$

So number of moles has increased by 2x

$$2x = 96 \text{ mm}$$

$$x = 48 \text{ mm.}$$

For a first order reaction,

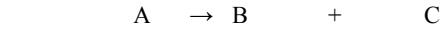
$$5.2 \times 10^{-4} = \frac{2.303}{320} \log_{10} \frac{a}{a - 48}$$

$$\text{Solving, } \log \frac{a}{a - 48} = 0.07225$$

Solving,

$$a = 313 \text{ mm.}$$

8. For a first order reaction



$$\text{At } t = 0 \quad a \quad 0 \quad 0$$

$$\text{At } t = t \quad a - X \quad X \quad X$$

$$\text{At } t = \infty \quad 0 \quad a \quad a$$

Suppose  $r_1^\circ$  and  $r_2^\circ$  are the specific rotations for B and C.

$$r_1 = X (r_1^\circ + r_2^\circ) = 50$$

$$\text{So } \frac{X = 50}{r_1^\circ + r_2^\circ}$$

$$r_\infty = a (r_1^\circ + r_2^\circ) = 100$$

$$a = \frac{100}{r_1^\circ + r_2^\circ}$$

$$k = \frac{2.303}{10} \log_{10} \frac{100}{50} = 0.069 \text{ min}^{-1}$$

10. At 450°C,

$$k = \frac{0.693}{t^{1/2}} = \frac{0.693}{10.17 \text{ min}}$$

$$= 0.0681 \text{ min}^{-1}$$

Now for 75 % decomposition

$$x = 75 \% \text{ of } a = 0.75 a$$

$$t = \frac{2.303}{k} \log \frac{a}{k a - x}$$

$$= \frac{2.303}{0.0681 \text{ min}^{-1}} \log \frac{a}{a - 0.75a}$$

$$= \frac{2.303}{0.0681 \text{ min}^{-1}} \log \frac{1}{0.25}$$

$$= 20.39 \text{ min}$$

11. As  $k \propto [a]^{1-n}$

For a first order reaction

$$k_1 \propto [a]^{1-1}$$

$$k_1 \propto 1$$

As k is constant and independent of unit of a, so  $k_1 = k'$

For second order reaction,

$$k_2 \propto 1/a$$

$$k_2 \propto \frac{1}{a \text{ mole dm}^{-3}} = \frac{1}{a \times 10^{-3} \text{ mole ml}^{-1}}$$

$$k'_2 \propto \frac{1}{a \text{ mole ml}^{-1}}$$

$$\text{So } k_2 = k'_2 \times 10^3 = k'_1$$

12.  $r = k [A] = 60 \times 10^{-4} \times 0.01$

$$= 60 \times 10^{-4} \times \frac{1}{10^2}$$

$$= 60 \times 10^{-6} \text{ mol L}^{-1} \text{ min}^{-1}$$

13. Suppose the number of radioactive nuclei is  $N_0$  at  $t = 0$ ,

The number of radioactive nuclei at a given instant 't' is  $N_0/4$ .

After  $t = 10$  sec, the number of undecayed nuclei reduces to 12.5% of  $N_0$  that is, becomes half of the  $N_0/4$ . It means  $t_{1/2}$  is 10 sec.

$$\frac{0.693}{10} = \frac{2.303}{t} \log_{10} \frac{N_0}{N_0 \times 6.25/100}$$

$$\frac{0.693}{10} = \frac{2.303}{t} \log \frac{100}{6.25}$$

$$t = \frac{2.303 \times 10}{0.693} \log_{10} 16 = 40 \text{ sec}$$

14.  $\ln k_1 = \ln A - 18/RT$ .

$$\ln k_2 = \ln A - 4/RT$$

$$\ln k_1 - \ln k_2 = -18/RT + 4/RT$$

$$= \frac{1}{RT} (4 - 18)$$

$$= -\frac{14 \text{ kJ}}{RT}$$

$$\log_{10} \frac{k_1}{k_2} = - \frac{14 \times 10^3}{2.303 \times 8.314 \times 300}$$

$$\text{so } k_1/k_2 = 3.656 \times 10^{-3}$$

15. According to

$$k = Ae^{-E_a/RT}$$

$$E_a = 0$$

$$k = Ae^0 = A$$

So the value of  $k$  at 280 K = the value of  $k$  at 300 K  
 $= 1.6 \times 10^{-6} \text{ s}^{-1}$

17.  $\Delta E^\circ = E_{a(f)} - E_{a(r)}$

This holds good for uncatalysed and catalysed reactions

$\Delta E^\circ$  is the same for both these reactions.

For the uncatalysed reaction, -30 kcal

$$= 28.0 \text{ kcal} - E_{a(r)}$$

$$\text{So } E_{a(r)} = 58.0 \text{ kcal}$$

For the catalysed reaction, -30 kcal

$$= 10.5 \text{ kcal} - E_{a(r)}$$

$$\text{So } E_{a(r)} = 40.5 \text{ kcal}$$

$$18. k = 5 \times 10^{11} \times \exp(-128000/RT)$$

$$= A \cdot \exp(-E_a/RT)$$

$$E_a = 128000 \text{ J mol}^{-1}$$

For gaseous reaction

$$\Delta H = E_a + (\Delta n - 1)RT,$$

Here  $\Delta n$  is change in the number of molecules, when the activated complex is formed.

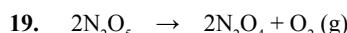
Here  $\Delta n = 0$  (unimolecular reaction).

$$\text{So } \Delta H = 128000 - 8.314 \times 448 \text{ J mol}^{-1}$$

$$= (128000 - 3725) \text{ J mol}^{-1}$$

$$= 124275 \text{ J mol}^{-1}$$

$$= 124.3 \text{ kJ mol}^{-1}$$



(solution) (solution)

The maximum volume of  $\text{O}_2$  gas obtainable is directly proportional to the initial concentration of  $\text{N}_2\text{O}_5$

that is  $100 \text{ cm}^3 \propto [\text{N}_2\text{O}_5]_0$

$90 \text{ cm}^3$  of  $\text{O}_2$  evolved is  $\propto \text{N}_2\text{O}_5$  decomposed

So  $(100 - 90)$  that is,  $10 \text{ cm}^3$  is  $\propto \text{N}_2\text{O}_5$  remaining that is  $10 \text{ cm}^3 \propto [\text{N}_2\text{O}_5]_t$

The first order rate constant

$$k = \frac{2.303}{500 \text{ min}} \log \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t}$$

$$= \frac{2.303}{500 \text{ min}} \log \frac{100}{10} = \frac{2.303 \text{ min}^{-1}}{500}$$

20. Rate of disappearance of  $\text{I}^-$ ,

$$\frac{-d[\text{I}^-]}{dt} = \frac{(0.20 - 0.18) \text{ mol L}^{-1}}{20 \text{ min}}$$

$$= 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$$

$$\text{Rate of reaction} = -\frac{1}{2} \frac{d[\text{I}^-]}{dt}$$

$$= + \frac{d[\text{I}_2]}{dt}$$

So rate of formation of  $\text{I}_2$ ,

$$\frac{d[\text{I}_2]}{dt} = -\frac{1}{2} \frac{d[\text{I}^-]}{dt} = \frac{10^{-3}}{2}$$

$$= 5 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$$

$$21. r = k [A]^a [B]^b \quad \dots \dots (1)$$

$$72 r = k [3A]^a [2B]^b \quad \dots \dots (2)$$

On dividing equation (2) by equation (1), we get

## 7.56 ■ Chemical Kinetics

$$72 = 3^a 2^b$$

Test by substituting the given values of a and b

When a = 2, b = 3, we get

$$3^a 2^b = 3^2 \times 2^3 = 9 \times 8 = 72.$$

22.  $t = 2.303 \log_{10} 100 = 127.7 \text{ sec}$

$$8.25 \times 10^{-4} 90$$

23.  $\lambda = \frac{2.303}{1600 \times 365 \times 24 \times 86400}$   
 $\times \frac{1 \times 6.023 \times 10^{23}}{226}$   
 $= 3.7 \times 10^{10}$

24. For a first order reaction,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}.$$

$$k = \frac{2.303}{60} \log_{10} \frac{100}{40} = \frac{2.303}{60} \times \log_{10} 2.5$$
  
 $= 0.0153$

$$t_{1/2} = \frac{2.303}{k} \log_{10} \frac{100}{50} = \frac{2.303}{0.0153} \times \log_{10} 2$$
  
 $= 45.31 \text{ min.}$

25. As  $k = Ae^{-E_a/RT}$

$$\ln k = \ln A - \frac{E_a}{RT}.$$

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303 RT}$$

$$\log_{10} A = \log_{10} k + \frac{E_a}{2.303 RT}$$

$$\log_{10} A = \log_{10} (1.8 \times 10^{-5}) + 15.7082$$

$$\log_{10} A = 0.2553 - 5 + 15.7082$$

$$= 10.9635$$

$$A = \text{Antilog} (10.9635)$$

$$A = 91.94 \times 10^{10} \text{ collision/sec.}$$

26. Suppose k and k' are the rate constants of the uncatalysed and catalysed reactions and Ea and E'a are their corresponding activation energies.

$$k = Ae^{-E_a/RT}$$

$$k' = Ae^{-E'a/RT}$$

$$\text{As } E'a = 4.15 \text{ kJ mol}^{-1}$$

$$\text{So } \frac{k'}{k} = e^{(E_a - E'a)/RT}$$

$$\text{As } k' = (1 + 1.718) k = 2.718 k = e \times k$$

$$\text{So } e = e^{(E_a - E'a)/RT}$$

$$Ea - E'a = RT$$

$$Ea = E'a + RT = 4.15 + 8.3 \times 500 \times 10^{-3}$$

$$= 8.3 \text{ kJ mol}^{-1}$$

$$\ln k = \ln A - \frac{E_a}{R} \times \frac{1}{T}.$$

$$\text{Slope} = -\frac{E_a}{R} = -\frac{8.3 \times 10^3}{8.3} = -1000$$



Initial moles 1

Moles after 1 - 0.2 0.4

disso. = 0.8

Total moles after dissociation

$$= 0.8 + 0.4 = 1.2$$

Initial temperature = 300 K

As  $P_1 V = n_1 RT_1$

$$1 \times V = 1 \times R \times 300 \quad \dots(1)$$

Temperature after dissociation = 600 K

$P_2 V_2 = n_2 RT_2$

$$P_2 \times V = 1.2 \times R \times 600 \quad \dots(2)$$

On dividing equation (2) by (1), we get

$$P_2 = \frac{1.2 \times 600}{300} = 2.4 \text{ atm}$$

28.  $k = Ae^{-E_a/RT}$  (Arrhenius equation)

when  $T \rightarrow \infty$

$$k = A e^0, \text{ or } k = A$$

$$\text{Thus } k = 6 \times 10^{14} \text{ s}^{-1}$$

29. Order =  $\frac{1}{2} + \frac{1}{3} + \frac{1}{4} = \frac{6+4+3}{12}$   
 $= 13/12$

30. According to hit and trial method, if reaction is of zero order,

$$k = \frac{1}{t} \{[A]_0 - [A]\}$$

Case I.

$$k = \frac{1}{25} \times \frac{25}{100} = 10^{-2}$$

Case II.

$$k = \frac{1}{25} \times \frac{1}{2} \{[A]_0 - [A]\}$$

$$= \frac{1}{25} \times \frac{1}{2} \times \frac{50}{100} = 10^{-2}$$

Case III.

$$k = \frac{1}{50} \times 2 \{[A]_0 - [A]\}$$

$$= \frac{1}{50} \times 2 \times \frac{25}{100} = 10^{-2}$$

As k is constant So the give reaction is of zero order.

# CHAPTER 8

# Solid State

## Chapter Contents

Classification of solids, crystalline state, seven crystal systems (cell parameters a, b, c, alpha, beta, gamma), close packed structure of solids (cubic), packing in fcc, bcc and hcp lattices; Nearest neighbours, ionic radii, simple ionic compounds, point defects and Various level of multiple-choice questions.

## SOLID STATE

Solid is the state of any matter in which constituents are firmly attached due to strong forces.

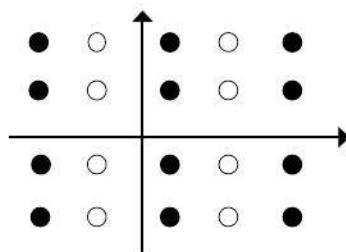
- Solids have a definite shape, mass and volume.
- Solids are almost incompressible, rigid and have mechanical strength.
- Solids have close packed arrangement of atoms.
- Solids have high density but very slow diffusion rate.
- Solids can have only vibrational motion as the constituents have fixed positions.
- In solids constituents have strong force of attraction as intramolecular distances are short.

## Type of Solids

Solids are mainly of the following two types:

## Crystalline Solids

In such solids, the constituents are arranged in a definite or orderly manner which repeats itself over long distances.



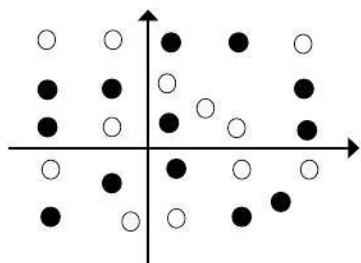
- They have a definite geometry with flat faces and sharp edges.
- Such solids have sharp melting points and undergo clean cleavage.
- They are considered as true solids.

## 8.2 ■ Solid State

- These show anisotropy that is, different physical properties in different directions.
- They show clean cleavage.
- They are normally incompressible. Example, Diamond, Quartz.
- All elements and compounds are of this kind.

### Amorphous Solids

In such solids, the constituents are not arranged in a regular or orderly manner over the long range.



### REMEMBER

Due to short range order, amorphous solids may even have small parts in crystalline and the rest in non-crystalline form. Crystalline parts of an otherwise amorphous substance are called crystallites.

### Types of Crystalline Solids

On the basis of nature of constituent particles and binding forces such solids are of following four types:

Type of Solids	Constituents Particles	Nature of Force	Physical State	M.P. in Kelvin	B.E. in kJ/mole	Conductivity	Examples
Ionic	Cations and anions	Strong electrostatic forces	Hard but brittle	Very high > 1300 K	400 – 4000	Conductors	NaCl, KCl, KNO <sub>3</sub> , CaO, LiF
Covalent or network	Atoms	Covalent bonds	Very hard	Very–very high >3900 K	150 – 500	Insulators	Diamond, SiC, SiO <sub>2</sub> , Quartz
Molecular	Molecules	Van der Waal's forces like London forces dipole-dipole interaction and hydrogen bonding	Soft	Low < 273 K	Low < 40	Insulators	Dry ice, I <sub>2</sub> , solid argon, P <sub>4</sub> , S <sub>8</sub> etc.,
Metallic	Atoms	Metallic bonds	Hard but malleable and ductile	High 800 ~ 1000	80 ~ 1000	Conductors	All metals and most of the alloys

## Terms Related to Crystals

### Crystal

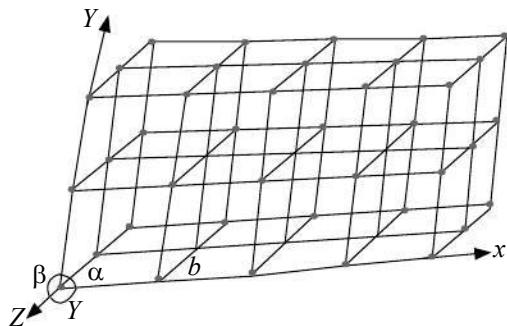
It is a homogeneous part of a solid substance made by regular pattern of structural units bonded by plane surface making definite angles with each other.

### Crystal Lattice or Space Lattice

It is the regular arrangement of constituent particles (atom, ions etc.,) of a crystal in three dimensional space.

### Face

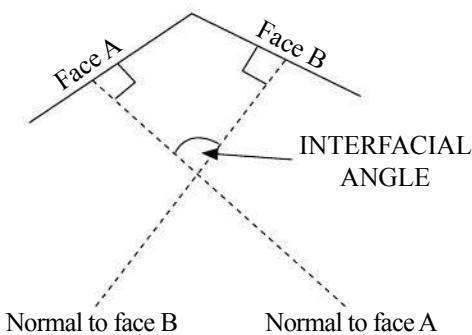
It is the plane surface of the crystal.



Space lattice and unit cell

### Edge

It is formed due to intersection of two adjacent faces.



### Interfacial Angles

It is the angle between the perpendiculars of two intersecting faces. When three or more edges intersect, a solid angle is formed.

### Unit Cell

It is the smallest unit or three dimensional portion of the space lattice which when repeated over and

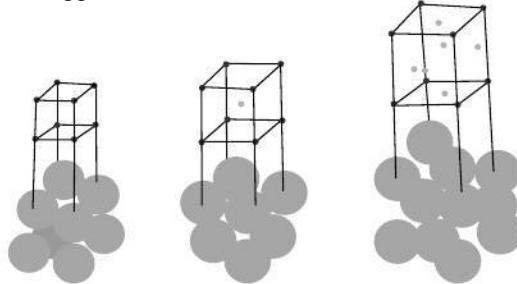
again in different directions give rise to the complete space lattice.

- It is the smallest geometrical figure having all the properties of a crystal in a crystal lattice.
- Any crystal may have  $\infty$  number of unit cells.
- It is characterized by  $a, b, c$  (edge distance) and  $\alpha, \beta, \gamma$ , (angles).

### Type of Unit Cell

Unit cells are of following types:

1. **Simple or Primitive or Basic Unit Cell:** Here lattice points or particles are present only at the corners and no where else. In this arrangement each atom is in contact with six immediate neighbouring species hence co-ordination number is six.
2. **Face Centered Unit Cell:** Here lattice points or particles are present not only at corners but also at the centre of each faces.
3. **Body Centered Unit Cell:** Here particles are present at all corners and centre of the body of the unit cell.
4. **End Face Centered:** Here particles are present at all corners as well as in the centre of two opposite faces.



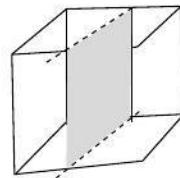
Simple cubic   Body-centred cubic   Face-centred cubic

### Types of Symmetry in Crystals

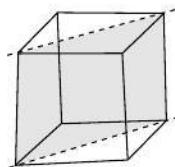
- A crystal may have center of symmetry plane of symmetry and axis of symmetry which can be explained as follows.
- Plane of symmetry is that imaginary plane which passes through the centre of the crystal and divide it into two equal portions (just mirror images of each other).
- Center of symmetry is an imaginary point which divides the surface of the crystal at equal distances in both directions by drawing any line through it. A crystal can have only one centre of symmetry.

## 8.4 ■ Solid State

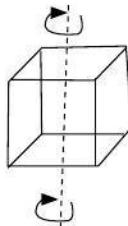
- Axis of symmetry is that imaginary straight line on which rotation of crystal gives similar appearance more than one time. It is two fold, three fold, four fold and six fold type respectively.



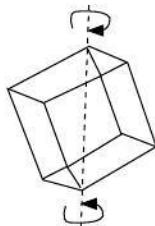
Rectangular plane of symmetry (a)



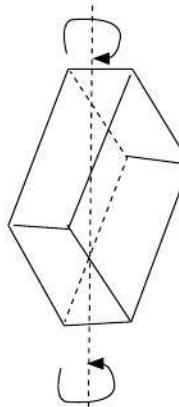
Diagonal plane of symmetry (b)



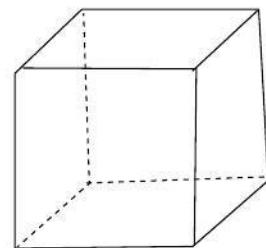
Axis of four-fold symmetry (c)



Axis of three-fold symmetry (d)



Axis of two-fold symmetry (e)



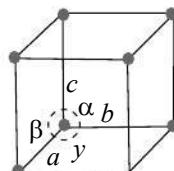
Centre of symmetry (f)

**Various elements of symmetry in a cubic crystal.**

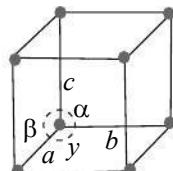
## CRYSTAL SYSTEMS

There are seven type of crystal systems and 14 bravais lattices as given below:

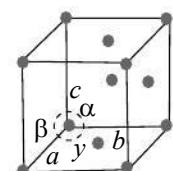
Crystal system	Bravais lattices	Parameters of Unit Cell			Examples
		Intercepts	Interfacial angle		
Cubic	Primitive, face centered, body centered = 3	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$		Ag, Au, Hg, Pb, diamond, NaCl, ZnS
Orthorhombic	Primitive, face centered, body centered, end centered = 4	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$		$K_2SO_4$ , $KNO_2$ , $BaSO_4$ Rhombic Sulphur
Tetragonal	Primitive, body centered = 2	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$		$TiO_2$ , $SnO_2$ , $CaSO_4$ White Tin
Monoclinic	Primitive, end centered = 2	$a \neq b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma \neq 90^\circ$		$CaSO_4 \cdot 2H_2O$
Triclinic	Primitive = 1	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$		$CuSO_4 \cdot 5H_2O$ , $K_2Cr_2O_7$ , $H_3BO_3$
Hexagonal	Primitive = 1	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$		Zn, Mg, Cd, $SiO_2$ Graphite, Zno
Rhombohedral	Primitive = 1	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$		Bi, As, Sb, $CaCO_3$ , $HgS$



Simple or Primitive (P)

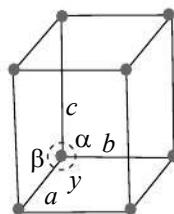


Body-centred (I)

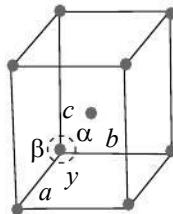


Face-centred (F)

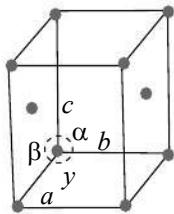
### Cubic Space Lattices



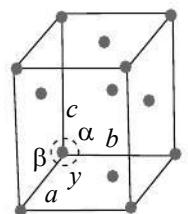
Simple or Primitive (P)



Body-centred (I)

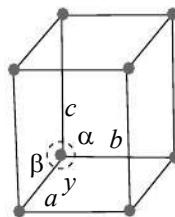


End-centred (C)

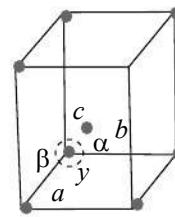


Face-centred (F)

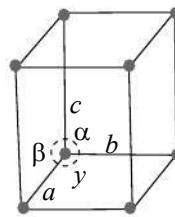
### Orthorhombic Space Lattices



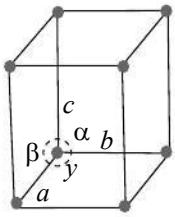
Simple (P)



Body-centred (I)

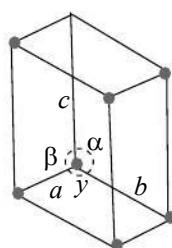


Simple (P)

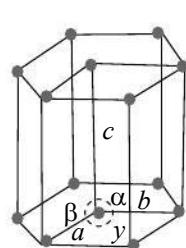


End-centred (C)

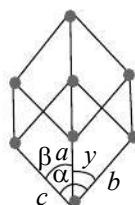
### Tetragonal and Monoclinic Space Lattices



Triclinic

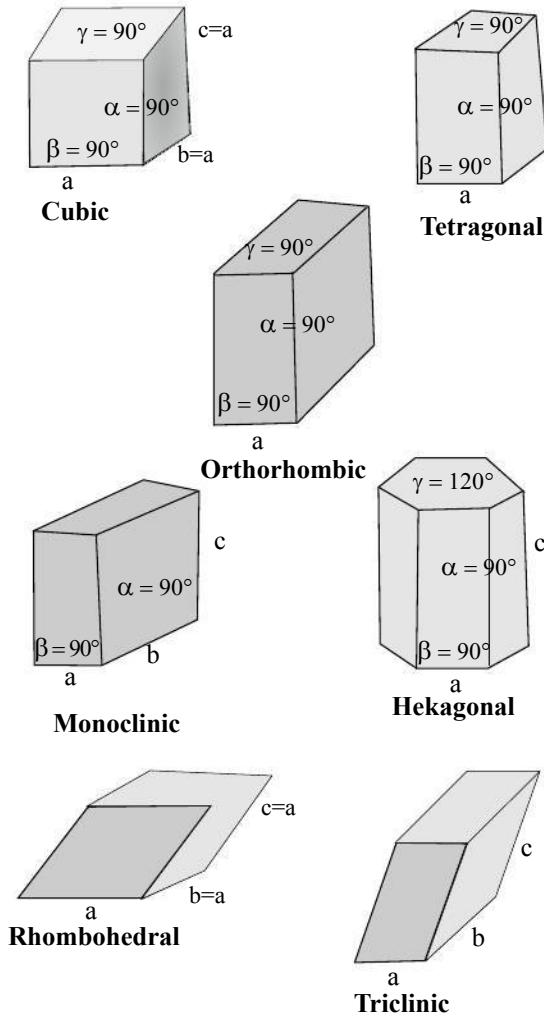


Hexagonal



Rhombohedral or Trigonal (R)

### Triclinic, Hexagonal and Rhombohedral Space Lattices



### Seven primitive unit cell in crystals

## Packing of Constituents in Crystals

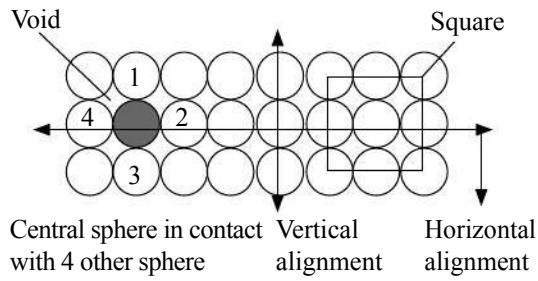
One can better understand the general geometrical requirements for crystal formation by considering various modes of packing in a number of identical spheres.

It is of the following two types:

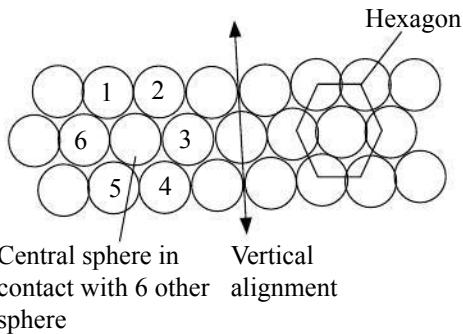
### Close Packing In Two Dimensions

Here close packing arrangement in two dimensions are as follows:

- (i) **Square Close Packing:** Here each sphere is in contact with four other spheres. Here voids are square. Here 52.4% space is occupied by spheres.



- (ii) **Hexagonal Close Packing:** It is more dense than the square Close packing. Here, voids are triangular and 60.4 % space is occupied by spheres.

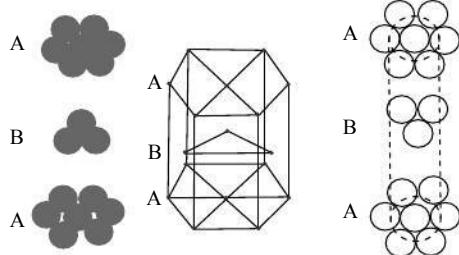


## Packing In Three Dimensions

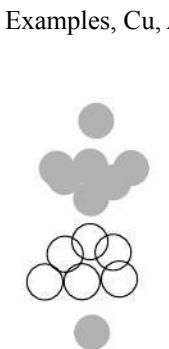
Atoms/Ions are space filling entities and structures can be described as resulting from the packing of spheres. The most efficient arrangement of spheres is called *closest packing*. In this kind of arrangement each sphere is in contact with the maximum possible number of adjacent neighbours. Here each sphere is surrounded by six nearest neighbours, lying in one plane, three spheres are just above it and some number are just below it also. This means the total number of nearest neighbours is twelve (Co. no=12). This kind of arrangement is further divided into H.C.P and C.C.P. arrangements. In order to obtain hexagonal close packing, first, spheres are placed on a flat surface to form layer (A) as shown in the figure (g). Now in order to form another another layer 'B' equally bunched spheres so as to nestle into the voids. From the given figure, it is clear that two types of voids (p,q) are formed. If a sphere is placed on the p-type of voids it resembles the A-layer of spheres. This kind of AB-AB type of arrangement is called H.C.P. If spheres are placed on q type of voids, it is another kind of unique layer let us call it 'C'- layer. It means ABC,.....ABC type of arrangement is formed which is called C.C.P.

**(i) Hexagonal Close Packing:**

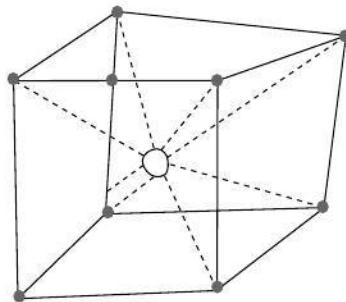
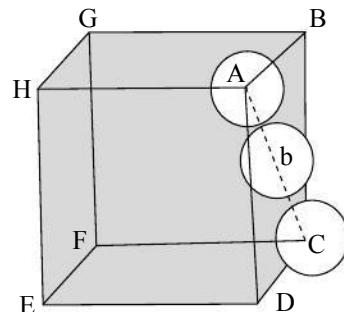
- Atoms are located at the corners and the center of two hexagons placed parallel to each other, three more atoms are placed in a parallel plane midway between these two planes. Here packing gives the arrangement of layers as AB, AB, ----. It has a six fold symmetry.
- Here 74 % space is occupied.
- Same appearance is obtained by rotating the crystal at  $60^\circ$ .
- Co-ordination is 12. Example, Mg, Zn, Mo, V, Cd.

**Arrangements in HCP****(ii) Cubic Close Packing:**

The sphere in the fourth layer will correspond to those in first layer and give rise to ABC, ABC, --- type of packing. It has 3 fold axis of symmetry which are passing through the diagonal of the cube. Here co-ordination number is 12.

**Arrangements in CCP****(iii) Body Centered Cubic Packing:**

Here each sphere is in contact with 8 spheres four in the lower layer and four in the upper layer. It is possible when the spheres in first layer are slightly opened that is, none of the sphere is touching each other. It is shown by Li, Na, K, Rb, Cs, Ba etc.,

**Packing Efficiency in HCP and CCP Structures**

**Cubic close packing-other sides are not provided with spheres for sake of clarity.**

Both types of close packing (hcp and ccp) are equally efficient. Let us calculate the efficiency of packing in ccp structure. In the figure, let the unit cell edge length be 'a' and face diagonal AC = b.

In  $\triangle ABC$

$$AC^2 = b^2 = BC^2 + AB^2$$

$$= a^2 + a^2 = 2a^2 \text{ or}$$

$$b = \sqrt{2}a$$

If r is the radius of the sphere, we find

$$b = 4r = \sqrt{2}a$$

$$\text{or } a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}r$$

$$(\text{We can also write, } r = \frac{a}{2\sqrt{2}})$$

As we know, that each unit cell in ccp structure, has effectively 4 spheres. Total volume of four spheres is equal to  $4 \times (4/3)\pi r^3$  and volume of the cube is  $a^3$  or  $(2\sqrt{2}r)^3$ .

Therefore,

## 8.8 ■ Solid State

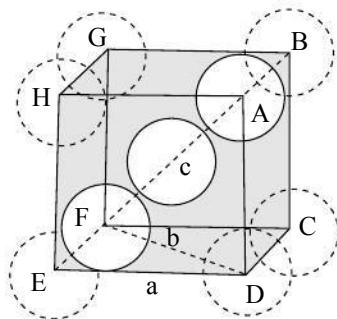
Packing efficiency =

$$\frac{\text{Volume occupied by four spheres in the unit cell} \times 100\%}{\text{Total volume of the unit cell}}$$

$$= \frac{4 \times (4/3) \pi r^3 \times 100}{(2\sqrt{2})^3} \%$$

$$= \frac{(16/3) \pi r^3 \times 100}{16\sqrt{2} r^3} = 74\%$$

### Efficiency of Packing in Body Centered Cubic Structure



**Body centred cubic unit cell (sphere alone the body diagonal are shown with solid boundaries).**

From figure, it is clear that the atom at the centre is in touch with the other two atoms diagonally arranged.

In  $\Delta EFD$ ,

$$b^2 = a^2 + a^2 = 2a^2$$

$$b = \sqrt{2}a$$

Now in  $\Delta AFD$

$$c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2$$

$$c = \sqrt{3}a$$

The length of the body diagonal  $c$  is equal to  $4r$ , here  $r$  is the radius of the sphere (atom), as all the three spheres along the diagonal touch each other.

So  $\sqrt{3}a = 4r$

$$a = \frac{4r}{\sqrt{3}}$$

Hence we can write,  $r = \frac{\sqrt{3}}{4} a$

In this type of structure, total number of atoms is 2

and their volume is  $2 \times \frac{(4)}{3} \pi r^3$

$$\text{Volume of the cube, } a^3 \text{ will be equal to } \frac{(4r)^3}{\sqrt{3}} \text{ or } a^3 = \frac{(4r)^3}{\sqrt{3}}$$

Therefore,

Packing efficiency

$$= \frac{\text{Volume occupied by two spheres in the unit} \times 100\%}{\text{Total volume of the unit cell}}$$

$$= \frac{4 \times (4/3) \pi r^3 \times 100}{[(4\sqrt{3})r]^3} \%$$

$$= \frac{4 \times (4/3) \pi r^3 \times 100}{64/(3\sqrt{3})r^3}\% = 68\%$$

### Interstitial Voids

It is the space left after different type of packings like hcp, ccp due to the spherical nature of atoms that is, the three dimensional interstitial gaps are called voids.

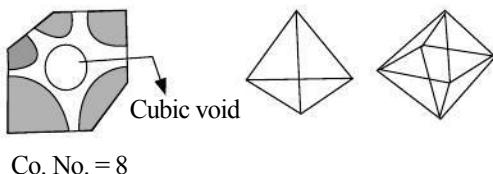
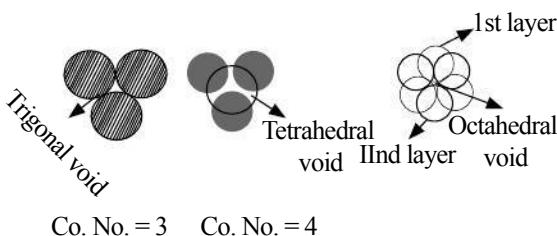
These are of the following types:

(i) **Trigonal Voids:** It is the vacant space touching three spheres that is, it is a two dimensional void formed when three spheres are in same plane whose centers are at corners of triangle.

(ii) **Tetrahedral Voids:** It is the vacant space touching four spheres that is the void whose surrounding spheres are located at the corners of regular tetrahedron. In general the number of these voids in a unit cell is double the number of effective atoms in that unit cell.

(iii) **Octahedral Voids:** It is the vacant space touching six spheres that is void resulting from overlapping of two trigonal voids of adjacent layer whose surrounding spheres are located at the corners of octahedron. In general, the effective number of these voids in a unit cell is equal to the number of effective atoms present in the unit cell.

(iv) **Cubic voids:** It is the vacant space touching eight spheres located at the corners of a cube.



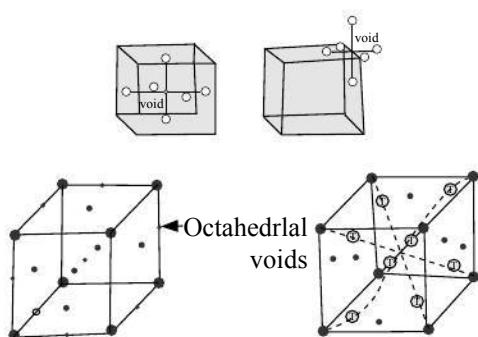
### Location of Voids in Unit Cell

- (i) **Tetrahedral Voids:** These voids are located at the body diagonals, two in each body diagonal at one fourth of the distance from each end. Total number of these voids per unit cell = 8
- (ii) **Octahedral Voids:** These voids are located at the middle of the cell edges and at the centre of cubic unit cell.

$$\text{Total number of octahedral voids} = \frac{1}{4} \times 12 + 1 \\ = 4$$

So in CCP, the total number of voids per unit cell  
= 8 + 4 = 12

(Tetrahedral) (Octahedral)



### Size of voids

$$V_{\text{oct}} = 0.414 X r$$

$$V_{\text{tet}} = 0.214 X r$$

$$V_{\text{tri.}} = 0.115 X r$$

$$V_{\text{oct}} > V_{\text{tetra}} > V_{\text{tri}}$$

Here  $r$  is the radius of the biggest sphere.

### Illustrations

1. A compound is formed by two elements M and N. The element N forms CCP and atoms of M occupy 1/3 rd of tetrahedral voids. What is the formula of the compound?

**Solution**    N in CCP =  $\frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$   
(corner)

$$\text{M in tetrahedral voids} = 8 \times \frac{1}{3} = \frac{8}{3}$$

$$\begin{aligned} \text{N : M} &= 4 : \frac{8}{3} = 12 : 8 \\ &= 3 : 2 \end{aligned}$$

Thus formula of the compound is  $M_2N_3$

2. In a cubic close packed structure (CCP) of mixed oxide, it is found that lattice has  $O^{2-}$  ions and one half of the octahedral voids are occupied by trivalent cations ( $X^{3+}$ ) and one eighth of the tetrahedral voids are occupied by divalent cations ( $Y^{2+}$ ). What is the formula of the mixed oxide?

**Solution**    Number of trivalent cation ( $X^{3+}$ )

$$= \frac{1}{2} \times 4 = 2$$

Number of divalent cation ( $Y^{2+}$ )

$$= \frac{1}{8} \times 8 = 1$$

$$\text{Number of } O^{2-} = \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4 \\ (\text{CCP})$$

(corner) (face)

Therefore formula is  $X_2YO_4$ .

3. A cubic solid is made up of two elements A and B. Atoms B are at the corners of the cube and A at the body centre:

- (i) What is the formula of the compound?  
(ii) What are the co-ordination numbers of A and B?

**Solution**

- (i) Number of atoms of A (present at corners) contributed per unit cell

$$= \frac{1}{8} \times 8 = 1 \text{ atom}$$

Number of atoms of B (present in the cube) contributed per unit cell = 1 atom

Ratio of atoms A and B in the unit cell = 1 : 1

So the formula of the compound = AB

- (ii) The co-ordination number of each element (A and B) is 8.

4. Calculate the number of atoms in a cubic based unit cell having one atom on each corner and two atoms on each body diagonal.

**Solution**

Number of atoms contributed by 8 corner atoms

$$\text{per unit cell} = \frac{1}{8} \times 8 = 1 \text{ atom}$$

As number of atoms contributed by one diagonal  
= 2 atoms

So number of atoms contributed by 4 diagonals  
=  $4 \times 2$  atoms = 8 atoms

Therefore, total number of atoms contributed per unit cell =  $1 + 8 = 9$  atoms.

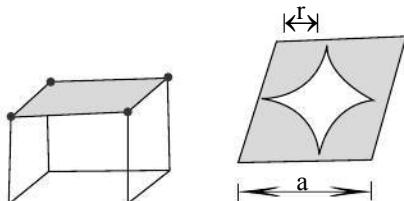
## Mathematical Analysis Of Cubic System

### 1. Atomic Radius and Edge Length

It is half of the distance between two nearest neighbour atoms in a crystal. It is expressed in terms of length of the edge (a) of the unit cell of a crystal.

#### (a) In Simple Cubic:

Here atoms located at corners are in contact.



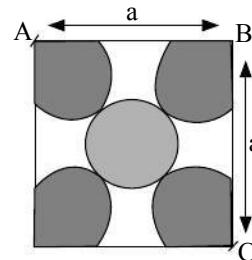
$$(i) a = 2r$$

- (ii) Distance between two nearer neighbour

$$= a/2 = r$$

$$\text{that is, } d = \frac{a}{2} = 2$$

#### (b) In face centered cubic (FCC):



Here atoms on face diagonal are in contact

$$\begin{aligned} \text{Face diagonal} &= r + 2r + r \\ &= 4r \end{aligned}$$

In triangle ABC

$$\begin{aligned} AC &= \sqrt{(AB^2 + BC^2)} \\ &= \sqrt{(a^2 + a^2)} \\ &= \sqrt{2} \times a \end{aligned}$$

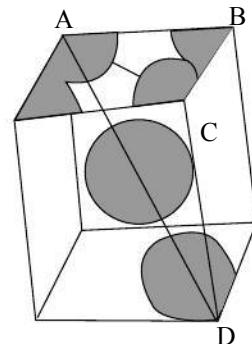
That is,  $4r = \sqrt{2} \times a$

$$(i) a = \frac{4r}{\sqrt{2}} = 2\sqrt{2} r$$

$$(ii) d = 2r$$

Here  $d$  = distance between two nearest atoms

#### (c) In Body Centered Cubic (BCC):



Here atoms on body diagonal are in contact that is,

$$\begin{aligned} \text{Body trigonal} &= r + 2r + r \\ &= 4r \end{aligned}$$

$$\begin{aligned} AD = BD &= 4r = \sqrt{(AC^2 + CD^2)} \\ &= \sqrt{[(a^2 + a^2) + a^2]} \\ 4r &= \sqrt{3} \times a \end{aligned}$$

$$(i) a = \frac{4r}{\sqrt{3}} \text{ for BCC}$$

$$(ii) d = 2r$$

Here  $d$  = distance between centers of two closest atoms

Property	Primitive	FCC	BCC
Diagonal	Facial $2\sqrt{2} r$	Facial $4r$	Body diagonal $4r$
Edge length	$2r = a$ $a = 2r$	$4r = \sqrt{2} a$ $a = \frac{4r}{\sqrt{2}} = 2\sqrt{2} r$	$4r = \sqrt{3} a$ $a = \frac{4r}{\sqrt{3}}$
Volume occupied by spheres	$1 \times \frac{4}{3} \pi r^3$	$4 \times \frac{4}{3} \pi r^3$	$2 \times \frac{4}{3} \pi r^3$
Volume of unit cell	$a^3 = 8a^3$	$a^3 = (2\sqrt{2} r)^3$	$a^3 = (4r/\sqrt{3})^3$
Packing fraction $= \frac{\text{Vol. occupied by atoms}}{\text{Vol. of unit cell}}$	$\frac{4/3 \pi r^3}{8 r^3} = 0.52$	$\frac{4 \times 4/3 \pi r^3}{(2\sqrt{2} r)^3} = 0.47$	$\frac{2 \times 4/3 \pi r^3}{(4r/\sqrt{3})^3} = 0.68$
Percentage of free space per unit cell	47.6 %	26 %	32 %

## 2. Number of Atoms Per Unit Cell or Unit Cell Content (Z)

- It is the total number of atoms contained in a unit cell for a simple cubic crystal.

$$Z = \frac{n_c}{3} + \frac{n_f}{2} + \frac{n_i}{1}$$

Here  $n_c = 3$ ,  $n_f = 6$ ,  $n_i = 1$

These are number of atoms at corner, face and inside body.

### In case of simple cubic crystal:

$$Z = 8 \times \frac{1}{8} = 1$$

As each corner atom is shared by eight surrounding cubes so it contributes for 1/8 of an atom.

### In face Centred Cubic Structure:

$$Z = 3 + 1 = 4$$

As the eight corners atom contribute for 1/8 of an atom that is, one atom per unit cell.

As each of 6 face centered atom is shared by two adjacent unit cells so one face centered atom contributes only half of its share that is,

$$6 \times \frac{1}{2} = 3 \text{ (atoms per unit cell)}$$

### In Body Centered Cubic Structure:

$$\text{Here } Z = 1 + 1 = 2$$

As eight corners atoms will contribute only one atom per unit cell and centre atom contributes only one atom per unit cell.

Address of an atom	Face of Cube	Corner of Cube	Body centre	Corner of Hexagonal	Side of Hexagonal	Edge of Cube
Contribution	$\frac{1}{2}$	$\frac{1}{8}$	1	$\frac{1}{6}$	$\frac{1}{2}$	$\frac{1}{4}$

## 3. Co-ordination Number (C. No.)

- It is equal to the number of nearest neighbours (atoms or ions) that is, touching Particles present around a species in a crystal. Its value gives us a measure of how tightly and closely the spheres are packed together the larger value of

its means more closer packing Its values depends upon the structure of crystal.

Example,

S.C. : Co-ordination number is 6

F.C.C : Co-ordination number is 12

B.C.C: Co-ordination number is 8

## 8.12 ■ Solid State

### 4. Density of Lattice Matter (d)

- It is the ratio of mass per unit cell to the total volume of a unit cell and it is find out as follows.

$$d = \frac{Z \times \text{Atomic weight}}{N_0 \times \text{Volume of unit cell} (a^3)}$$

Here  $d$  = Density

$Z$  = Number of atoms

$N_0$  = Avogadro number

$a^3$  = Volume

$a$  = Edge length

Here in order to find density of unit cell in g/cm<sup>3</sup>, m must be taken in g/mole and should be in cm.

### 5. Packing Fraction

- It is the ratio of the volume occupied by spheres or effective atoms in a unit cell to the total volume of that unit cell. The fraction volume of the unit cell, that is empty is known as void fraction.

$$\text{P.F.} = \frac{Z \times 4/3 \pi r^3}{a^3}$$

#### ■ In Simple Cubic:

$$\text{P.F. (f)} = \frac{4/3 \pi r^3}{(2r)^3} = 0.52 = 52\%$$

As  $a = 2r$

% void = 48 %

#### ■ In Body Centered Cubic:

$$\text{P.F.} = \frac{2 \times 4/3 \pi r^3}{(4r/\sqrt{3})^3} = 0.68 = 68\%$$

As  $a = 4r/\sqrt{3}$

% void = 32 %

#### ■ In Face Centered Cubic:

$$\text{P.F.} = \frac{4 \times 4/3 \pi r^3}{(4r/\sqrt{2})^3} = 0.74 = 74\%$$

As  $a = 4r/\sqrt{2}$

% void = 26 %

- (6) **Radius Ratio:** ( $R_i = r^+ / r^-$ ) It is the ratio of radius of octahedral void to the radius of sphere forming the close packed arrangement Normally ionic solids are more compact as voids are also occupied by cation (smaller in size) pattern of arrangements and type of voids both depend upon relative size (ionic size) of two ions in solid.

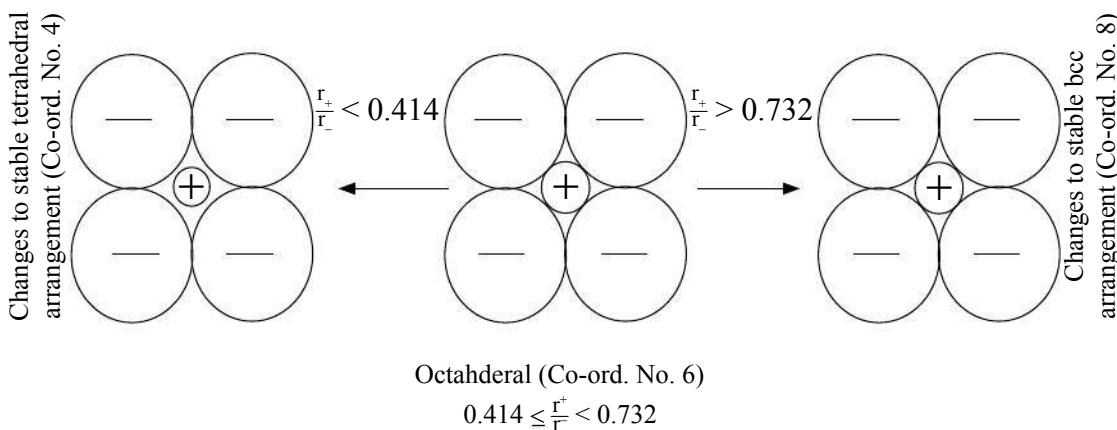
Example, when  $r^+ = r^-$  the most probable and favourable arrangement is BCC type.

With the help of a relative ionic radii, it is easier to predict the most probable arrangement. This property is expressed as radio ratio.

$$\text{Radius ratio} = \frac{r^+ (\text{radius of cation})}{r^- (\text{Radius of anion})}$$

From the value of radius ratio it is clear that larger the radius ratio larger is the size of cation and more will be the number of anions needed to surround it, that is, more co-ordination number.

Shape	Radius-ratio	Co-ordination number
For cubic	0.732-1.000	8
For octahedral	0.414-0.732	6
For tetrahedral	0.225-0.414	4
For triangular	0.155-0.225	3



**(i) Radius ratio for tetrahedron**

(co-ordination number 4)

Angle ABC is the tetrahedral angle of  $109.5^\circ$ 

$$\angle ABD = \frac{109.5}{2} = 54.75^\circ$$

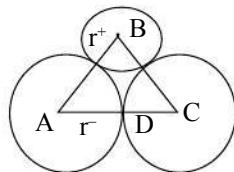
In triangle ABD,

$$\sin ABD = 0.8164 = AD/AB$$

$$= \frac{r^-}{r^+ + r^-}$$

$$\text{or } \frac{r^+ + r^-}{r^-} = \frac{1}{0.8164} = 1.225$$

$$\text{or } \frac{r^+}{r^-} = 0.225$$

**(ii) Radius ratio for octahedron**

$$AB = r^+ + r^-$$

$$BD = r^-$$

$$\angle ABC = 45^\circ$$

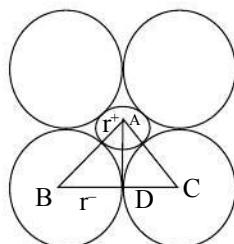
In triangle ABD

$$\cos ABD = 0.7071 = BD/AB$$

$$= \frac{r^-}{r^+ + r^-}$$

$$\text{or } \frac{r^+ + r^-}{r^-} = \frac{1}{0.7071} = 1.414$$

$$\text{or } \frac{r^+}{r^-} = 0.414$$

**Illustrations**

5. Find the close-packed structure of an ionic compound  $X^+Y^-$  in which the radius of the cation = 148 pm and the radius of anion = 195 pm. What is the co-ordination number of cation?

**Solution** Radius ratio =  $r^+/r^-$ .

$$= \frac{148}{195} = 0.759$$

As the value of radius ratio (0.759) is more than 0.732, the crystalline solid  $X^+Y^-$  has body centered cubic lattice.The co-ordination number of  $X^+ : Y^- :: 8 : 8$ 

6. A solid  $X^+ Y^-$  has NaCl type close packed structure. If the anion has a radius of 241.5 pm, what should be the minimum radius of the cation? Can a cation,  $Z^+$  having radius of 50 pm be fitted into the tetrahedral hole of the crystal  $X^+ Y^-$ ?

**Solution** Radius ratio for an octahedral hole

$$= \frac{r^+}{r^-} = \frac{\text{Size of the cation } X^+}{\text{Size of the anion } Y^-} = 0.414$$

$$r^+ = 0.414 r^- = 0.414 \times 241.5 = 99.98 \text{ pm.}$$

$$\text{For a tetrahedral hole} = \frac{r^+}{r^-} = 0.225$$

The minimum radius of the cation  $X^+$  to fit exactly into the octahedral hole should be 99.98.

$$r^+ = 0.225 r^- = 0.225 \times 241.5 = 54.34 \text{ pm}$$

As the size of the cation  $Z^+$  (50 pm) is less than the ideal radius (54.34 pm), it can be fitted into tetrahedral hole of the crystal  $X^+ Y^-$ .

7. In crystalline solid, anion Z are arranged in cubic close packing, cations X occupy 50 per cent of the tetrahedral voids and cations Y occupy 50 percent of octahedral voids. What is the formula of the solid?

**Solution** Suppose the number of anions, Z = 100.

Number of cations, X

$$= \frac{50}{100} \times \text{Number of octahedral void}$$

## 8.14 ■ Solid State

$$\begin{aligned} &= \frac{50}{100} \times (2 \times \text{Number of anions } Z) \\ &= \frac{50}{100} \times 2 \times 100 = 100 \end{aligned}$$

Number of Cations, Y

$$\begin{aligned} &= \frac{50}{100} \times \text{Number of octahedral void} \\ &= \frac{50}{100} \times \text{Number of anions } Z \\ &= \frac{50}{100} \times 100 = 50 \end{aligned}$$

Ratio of ions : A : B : C = 100 : 50 : 100

$$= 2 : 1 : 2$$

So, formula of the compound is  $A_2BC_2$

8. Copper which crystallizes as a face-centered cubic lattice has a density of 8.930 g/cm<sup>3</sup> at 20°C.

- (i) Calculate the length of the unit cell.
- (ii) Calculate the radius of a copper atom.

**Solution** The number of atoms per unit cell is 4 as copper crystallizes as face centered cubic lattice.

Z = 4 atoms/unit cell,

Atomic mass of copper = 63.5 g/mol.

$$\text{Density} = \frac{\text{Atomic mass} \times Z}{\text{Unit cell volume (cm)}^3 \times N_0}.$$

$$\text{Unit cell volume} = \frac{\text{Atomic mass} \times Z}{\text{Density} \times N_0}.$$

$$= \frac{63.5 \times 4}{8.930 \times 6.023 \times 10^{23}} = 4.722 \times 10^{-23} \text{ cm}^3/\text{unit cell}$$

Length of side of the unit cell =  $(V \text{ cm}^3)^{1/3}$

$$= [4.722 \times 10^{-23}]^{1/3}$$

$$= 3.616 \times 10^{-8} \text{ cm}$$

$$= 3.616 \times 10^{-8} \times \frac{10^{10} \text{ pm}}{1 \text{ cm}}$$

$$= 361.6 \text{ pm}$$

For a face centered cubic lattice,  $a = \sqrt{3}r$

$$r = \frac{a}{\sqrt{3}} = \frac{361.6 \text{ pm}}{\sqrt{3}} = 128 \text{ pm.}$$

9. An element crystallizes in BCC structure. The edge of its unit cell is 288 pm. If the density of the crystals is 7.2 g cm<sup>-3</sup>. What is the atomic mass of the element?

**Solution** As the element has BCC structure so number of atoms per unit cell is 2.

Length of edge of the unit cell = 288 pm

$$= 288 \times \frac{1 \text{ cm}}{10^{10} \text{ pm}} = 288 \times 10^{-10} \text{ cm}$$

$$\text{Volume of the unit cell} = (288 \times 10^{-10} \text{ cm})^3$$

$$= 2.4 \times 10^{-23} \text{ cm}^3$$

$$\text{Density} = \frac{\text{Atomic mass} \times Z}{\text{Unit cell volume} \times N_0}.$$

$$\text{Atomic mass} = \frac{\text{Density} \times \text{Unit cell volume} \times N_0}{Z}$$

$$= \frac{7.2 \times 2.4 \times 10^{-23} \times 6.023 \times 10^{23}}{2}$$

$$= 52 \text{ g mol}^{-1}$$

10. An element crystallizes in FCC structure. Its density is 7.2 g cm<sup>-3</sup>. 208 g of this element has  $4.283 \times 10^{24}$  atoms. Calculate the edge length of the unit cell.

**Solution** Molar mass = Mass of  $6.023 \times 10^{23}$  atoms

$$\text{Mass of } 4.283 \times 10^{24} \text{ atoms} = 208 \text{ g}$$

$$\text{Atomic mass} = \text{Mass of } 6.023 \times 10^{23} \text{ atoms}$$

$$= \frac{208 \times 6.023 \times 10^{23}}{4.283 \times 10^{24}} = 29.25 \text{ g/mol}$$

$$\text{Density} = \frac{\text{Atomic mass} \times Z}{V (\text{cm})^3 \times N_0}$$

$$\text{Unit cell volume} = \frac{\text{Atomic mass} \times Z}{\text{Density} \times N_0}$$

$$= \frac{29.25 \times 4}{7.2 \times 6.023 \times 10^{23}} = 26.98 \times 10^{-24} \text{ cm}^3$$

$$a = (V)^{1/3} = \sqrt[3]{(26.98 \times 10^{-24})} = 3 \times 10^{-8} \text{ cm.}$$

11. Tungsten has a density of 19.35 g cm<sup>-3</sup> and the length of the side of the unit cell is 316 pm. The unit cell in the most important crystalline form of tungsten is the body-centered cubic unit cell. How many atoms of the element does 50 g of the element contain?

**Solution**

$$\text{Length of edge of the unit cell} = 316 \text{ pm}$$

$$= 316 \times \frac{1 \text{ cm}}{10^{10} \text{ pm}} = 316 \times 10^{-10} \text{ cm}$$

$$\begin{aligned}\text{Volume of the unit cell} &= (316 \times 10^{-10} \text{ cm})^3 \\ &= 3.2 \times 10^{-23} \text{ cm}^3/\text{unit cell}\end{aligned}$$

$$\text{Density} = \frac{\text{Atomic mass} \times Z}{\text{Unit cell volume} \times N_0}$$

$$\begin{aligned}\text{Atomic mass} &= \frac{\text{Density} \times \text{Unit cell volume} \times N_0}{Z} \\ &= \frac{19.35 \times 3.2 \times 10^{-23} \times 6.023 \times 10^{23}}{2} = 186.5 \text{ g/mol}\end{aligned}$$

As 186.5 g of the element contains  $N_0$  atoms  
 $= 6.023 \times 10^{23}$  atoms

$$\begin{aligned}\text{So } 50 \text{ g of the element contain } N_0 \text{ atoms} \\ &= 6.023 \times 10^{23} \times \frac{50}{186.5} \\ &= 1.614 \times 10^{23} \text{ atoms}\end{aligned}$$

12. Given for Fe:  $a \text{ pm} = 286$ ,  $\rho \text{ g cm}^{-3} = 7.86$ . Find the type of cubic lattice to which the crystal belongs. Also calculate the radius of Fe. (Atomic weight of Fe = 55.85).

**Solution** Length of edge of the unit cell = 286 pm

$$= 286 \times \frac{1 \text{ cm}}{10^{10} \text{ pm}} = 286 \times 10^{-10} \text{ pm}$$

$$\begin{aligned}\text{Volume of the unit cell} &= (286 \times 10^{-10} \text{ cm})^3 \\ &= 2.34 \times 10^{-23} \text{ cm}^3\end{aligned}$$

$$Z = \frac{\text{Unit cell volume} \times \text{Density} \times N_0}{\text{Molar mass of Fe}}$$

$$= \frac{2.34 \times 10^{-23} \times 7.86 \times 6.023 \times 10^{23}}{55.85} = 2$$

As the number of atoms per unit cell is 2, iron has body centered cubic crystal structure.

$$a = \frac{2}{\sqrt{3}} \cdot d = \frac{2}{\sqrt{3}} (2r)$$

$$r = \frac{\sqrt{3}}{\sqrt{3}} \times a = \frac{\sqrt{3}}{4} \times 286 = 123.8 \text{ pm.}$$

13. Potassium fluoride has the NaCl type structure. The density of KF is  $2.48 \text{ g/cm}^3$  at  $20^\circ\text{C}$ . (i) Calculate the unit cell length, (ii) Calculate the nearest neighbour distance in KF.

**Solution** Formula mass of KF =  $39 + 19 = 58$  amu

NaCl has face centered cubic lattice. The number of formula units (ion-pairs) per unit cell of NaCl or KF is 4 as it has a face centered cubic lattice.

$$Z = 4 \text{ formula unit/unit cell}$$

$$\text{Density} = \frac{\text{Formula mass} \times Z}{\text{Unit cell volume} \times N_0}$$

$$\text{Unit cell volume} = \frac{\text{Formula mass} \times Z}{\text{Density} \times N_0}$$

$$\begin{aligned}\text{Unit cell volume} &= \frac{58 \times 4}{2.48 \times 6.023 \times 10^{23}} \\ &= 1.553 \times 10^{-22} \text{ cm}^3/\text{unit cell}\end{aligned}$$

$$\begin{aligned}\text{Unit cell length} &= (V)^{1/3} = (1.553 \times 10^{-22} \text{ cm}^3)^{1/3} \\ &= 5.377 \times 10^{-8} = 537.7 \text{ pm}\end{aligned}$$

The nearest neighbour distance is shortest distance between any two ions in the lattice. In a FCC unit cell of the compound of the type AB, the side of the cube contains  $\frac{1}{2}$  ion of A, 1 ion of B and  $\frac{1}{2}$  ion of A. Thus length of the side of the unit cell is twice the nearest neighbour distance.

The nearest neighbour distance in KF

$$\begin{aligned}&= \frac{\text{Length of the side of unit cell}}{2} \\ &= \frac{537.7}{2} = 268.9 \text{ pm.}\end{aligned}$$

14. An element 'X' (atomic mass 100) having BCC structure has unit cell edge 400 pm. Calculate the density of X and the number of unit cells for 10 g of X. ( $N_0 = 6.023 \times 10^{23}$ )

**Solution** Length of the unit cell edge = 400 pm

$$= 400 \times \frac{1 \text{ cm}}{10^{10} \text{ pm}} = 400 \times 10^{-10} \text{ cm}$$

$$\begin{aligned}\text{Volume of the unit cell} &= (400 \times 10^{-10} \text{ cm})^3 \\ &= 6.4 \times 10^{-23} \text{ cm}^3\end{aligned}$$

As element 'X' forms a body centered cubic lattice so number of atoms per unit cell is 2.

$$Z = 2 \text{ atoms/unit cell}$$

$$\text{Atomic mass of the element} = 100 \text{ g/mol}$$

$$\text{Density of element} = \frac{\text{Atomic mass} \times Z}{\text{Unit cell volume} \times N_0}.$$

## 8.16 ■ Solid State

$$\frac{100 \times 2}{6.4 \times 10^{-23} \times 6.023 \times 10^{23}} = 5.188 \text{ g/cm}^3$$

$$\begin{aligned}\text{Volume of 10 g of X} &= \frac{\text{Mass}}{\text{Density}} \\ &= \frac{10}{5.188} = 1.9275 \text{ cm}^3\end{aligned}$$

Number of unit cells in  $1.9275 \text{ cm}^3$  volume

$$\begin{aligned}&= \frac{\text{Volume of the substance}}{\text{Unit cell volume}} \\ &= \frac{1.9275}{6.4 \times 10^{-23}} = 3.0 \times 10^{22} \text{ unit cells}\end{aligned}$$

- 15.** From the following data calculate the Avogadro number, sodium chloride crystal exists as a face-centered cube. The density of sodium chloride is  $2.164 \text{ g ml}^{-1}$  and the distance between  $\text{Na}^+$  and  $\text{Cl}^-$  ions from X-ray analysis was found to be  $2.818 \text{ \AA}$ .

**Solution** The distance between  $\text{Na}^+$  and  $\text{Cl}^-$  ions ( $d$ )

$$= 2.818 \text{ \AA} = 2.818 \times 10^{-8} \text{ cm}$$

The length of the unit cell for the face-centered cubic crystal =  $l = 2d = 2 \times 2.818 \times 10^{-8} \text{ cm}$ .

$$\begin{aligned}\text{Volume (V) of the unit cell} &= l^3 = (2 \times 2.818 \times 10^{-8})^3 \\ &= 1.792 \times 10^{-22} \text{ ml}\end{aligned}$$

$$\text{Volume of the unit cell} = \frac{M \times 4}{D \times N}$$

Here  $M$  = molecular weight of the substance

$D$  = Density

$N$  = Avogadro number

$$1.792 \times 10^{-22} \text{ ml} = \frac{58.44 \times 4}{2.164 \times N}$$

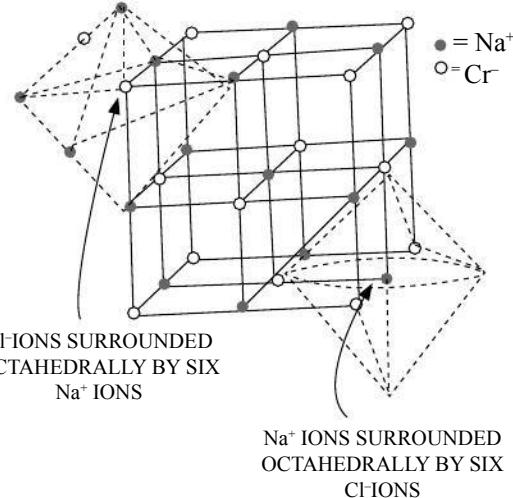
$$N = \frac{58.44 \times 4}{2.164 \times 1.792 \times 10^{-22}} = 6.026 \times 10^{23}$$

## Structure of Some Ionic Solids

### 1. Rock Salt (NaCl type):

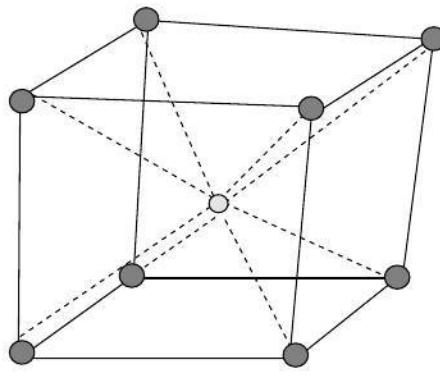
- In it  $\text{Cl}^-$  ions has C.C.P. structure that is, F.C.C. and  $\text{Na}^+$  ions occupies octahedral holes (voids) here.
- Both  $\text{Na}^+$  and  $\text{Cl}^-$  have co-ordination number six. Number of formula units per unit cell are four. Example, Halides of Alkali metals (except  $\text{CsX}$ ) like  $\text{LiX}$ ,  $\text{NaX}$ ,  $\text{KX}$ , other halides like  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{NH}_4\text{Cl}$  and oxides like  $\text{TiO}$ ,  $\text{FeO}$ ,  $\text{NiO}$ .

- $r_e + r_a = a/2$   $r_{\text{Na}^+}/r_{\text{Cl}^-}$  must be 0.414 however, it is 0.525.



### 2. CsCl – Type:

- Here  $\text{Cl}^-$  ions are at the corners of a cube and  $\text{Cs}^+$  ions are in the cubic void (centered position) i.e.B.C.C like structure.
- Here co-ordination number of both  $\text{Cs}^+$  and  $\text{Cl}^-$  is 8 and here number of formula units per unit cell is  $1.r_e + r_a = \sqrt{3}/2$
- Here  $r_{\text{Cs}^+}/r_{\text{Cl}^-}$  should be 0.732 but it is 0.93. e.g.  $\text{CsX}$ ,  $\text{TiCl}$ ,  $\text{TiBr}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$ .



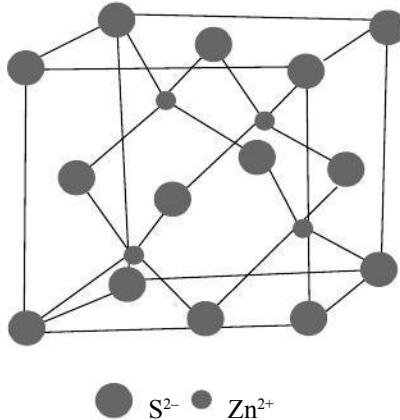
### 3. Zinc Blende (ZnS Type):

- Here  $\text{S}^{2-}$  occupies C.C.P or f.C.C arrangement while  $\text{Zn}^{2+}$  ions occupy alternate tetrahedral voids.

- Only half of the total voids is occupied.
- Here co-ordination number of both  $Zn^{2+}$  and  $S^{2-}$  is four and here number of formula units per unit cell is four.

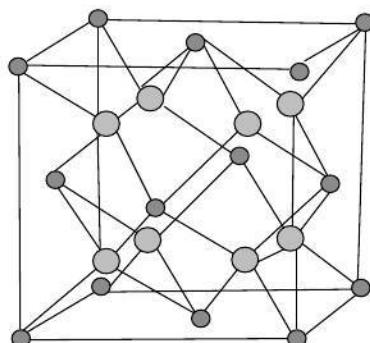
Example, ZnS, Beo CuCl, CuBr, CuI, AgI etc.,

$$r_e + r_a = \sqrt{3} \frac{a}{4}$$



#### 4. Fluorite Structure ( $CaF_2$ Type)

- Here  $Ca^{2+}$  occupies C.C.P and  $F^-$  ions occupy all the tetrahedral voids.
- Here coordination number of  $Ca^{2+}$  is 8 while for  $F^-$  it is four and the effective number of  $Ca^{2+}$  and  $F^-$  ions in a unit cell are 4 and 8 respectively here number of formula units per unit cell is four.  
 $r_e + r_a = \sqrt{3} \frac{a}{4}$



Example,  $CaF_2$ ,  $BaCl_2$ ,  $BaF_2$ ,  $SrF_2$ ,  $CO_2$ ,  $ThO_2$ ,  $PbO_2$  etc.

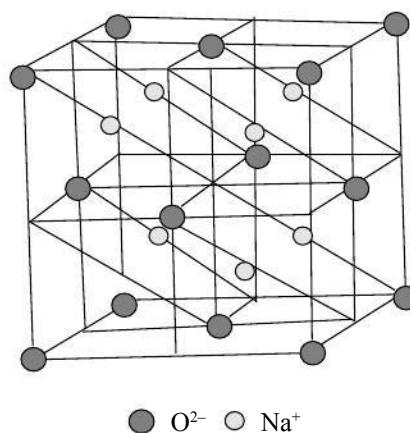
#### 5. Anti-fluorite Structure ( $Na_2O$ Type):

- Here negative ions ( $O^{2-}$ ) occupy C.C.P. while cations ( $Na^+$ ) occupy all the tetrahedral voids.
- Here co-ordination number of  $Na^+$  is four while for  $O^{2-}$  it is eight here number of formula units per unit

cell is four and the effective number of  $Li^+$  and  $O^{2-}$  ions in a unit cell are 8, and 4 respectively.

$$r_e + r_a = \sqrt{3} \frac{a}{4}$$

Example,  $Na_2O$   $K_2O$ ,  $Li_2O$  etc.,



$Na_2O$  Structure is an example of antifluorite structure.

#### Normal Spinal Structure ( $XY_2O_4$ )

- Spinal is  $MgAl_2O_4$  and spinals in general have the formula  $AB_2O_4$ . Here A is divalent cation ( $Mg^{2+}$ ,  $Ca^{2+}$ ) and B is trivalent cation ( $Al^{3+}$ ).
- Here  $Mg^{2+}$  occupy tetrahedral voids while oxide ions  $1/8$  of  $Al^{3+}$  occupy  $1/2$  octahedral voids.

I II I II I II

- Ferrites  $[ZnFe_2O_4]$   $FeFe_2O_4$ ,  $MnMn_2O_4$ ,  $FeCr_2O_4$  also have this type of structure.
- As magnetic materials these are used in telephones, memory loops of computers.

#### Inverse Spinal Structure ( $Fe_3O_4$ , Magnetite)

- In  $Fe_3O_4$ ,  $Fe^{3+}$  and  $Fe^{2+}$  are present in  $2 : 1$  ratio.
- Here oxides ions are in C C P while  $Fe^{2+}$ , ions occupy octahedral voids while  $Fe^{3+}$  occupy octahedral and tetrahedral voids.
- Here  $O^{2-}$  ions forms FCC unit cell.

Here the formula ratio of

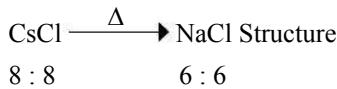
$$Fe^{2+} : Fe^{3+} : O^{2-} = 1 : 2 : 4$$

## 8.18 ■ Solid State

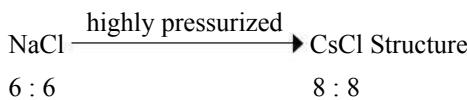
- $\text{MgFe}_2\text{O}_4$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{Mn}_3\text{O}_4$  have also this type of structure.

### Effect of Temperature and Pressure on Crystal Structure

- (i) On increasing the temperature of CsCl structure co-ordination number decreases from 8 : 8 to 6 : 6.



- (ii) On subjecting the NaCl structure to high pressure it will increase co-ordination number from 6 : 6 to 8 : 8.



### Imperfections in Solid

Any deviation from the perfectly ordered arrangement constitutes a defect or imperfection. These defects are sometimes called thermodynamic defects because the number of these defects depend on the temperature.

- Crystals may also possess additional defects due to the presence of impurities. Imperfection not only modify the properties of solids but also gives rise to new properties.

**Electronic Imperfection:** Generally electrons are present in fully occupied lowest energy states but at high temperatures, some of the electrons may occupy higher energy states depending upon the temperature.

- For example, in the crystals of pure Si or Ge some electrons are released thermally from the covalent bonds at temperature above 0 K. These electrons are free to move in the crystal and are responsible for electrical conductivity. This type of conduction is known as intrinsic conduction.
- The electron deficient bond formed by the release of an electron is called a hole. In the presence of electric field, the positive holes move in a direction opposite to that of the electrons and conduct electrically.

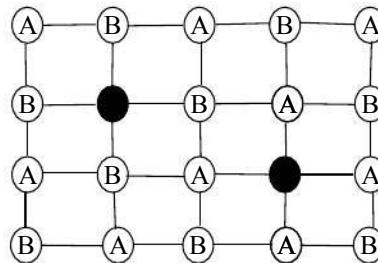
**Atomic Imperfection:** The compounds in which the number of irregularity present in the

arrangement of atoms or ions are called atomic imperfections. It is of two types:

- (i) **Stoichiometric Defects:** Those compounds in which the number of positive and negative ions are exactly in the ratio indicated by their chemical formula are called stoichiometric compounds example, NaCl.

These solids show following types of defects:

#### (a) Schottky Defect

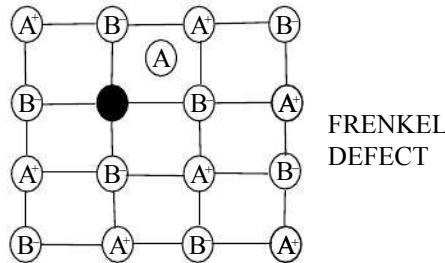


SCHOTTKY DEFECT

This type of defect is created when same number of positive ions and negative ion are missing from their respective positions leaving behind a pair of holes. Schottky defect is more common in ionic compounds with high co-ordination number and where the size of positive and negative ions are almost equal.

- This defect decreases density of crystals, however, it maintains electrical neutrality example, NaCl, CsCl, KCl, KBr etc.

#### (b) Frenkel Defect



FRENKEL DEFECT

This type of defect is created when an ion leaves its correct lattice site and occupies an interstitial site.

- Frenkel defects are common in ionic compounds which have low co-ordination number and in which there is large difference in size between positive

and negative ions or when the crystal structure is of an open type with large interstitial spaces.

Example, ZnS, AgCl, AgBr, AgI etc.

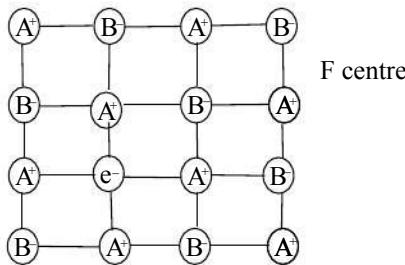
- (ii) Non Stoichiometric Defect:** There are many compounds in which the ratio of positive and negative ions present in the compound differs from the required by ideal formula of the compound. Such compounds are called Non stoichiometric compounds.

Example, VO<sub>x</sub>

- In these compounds, a balance of positive and negative charges is maintained by having extra electrons or extra positive charge.

These defects are of following types:

**(a) Metal Excess Defects due to Anion Vacancies**



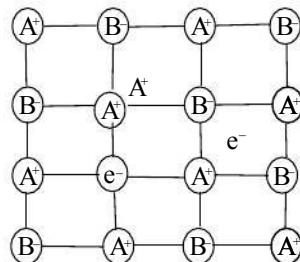
A compound may have excess metal ion if a negative ion is absent from its lattice site, leaving a hole which is occupied by an electron to maintain electrical neutrality.

- The holes occupied by electrons are called F-centres and are responsible for the colour of the compound.

Example,

- The excess of sodium in NaCl makes the crystal to appear yellow.
- Excess of potassium in KCl makes it violet.
- Excess of lithium in LiCl makes it pink.
- Greater the number of F-centres greater is the intensity of colour. This type of defects are found in crystal which are likely to possess schottky defects.

**(b) Metal Excess Defects due to Interstitial Cations:**



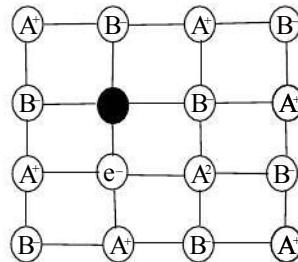
- It may occur if an extra positive ion is present in an interstitial site.
- Electrical neutrality is maintained by the presence of an extra electron in the interstitial site.
- This types of defects are exhibited by the crystals which are likely to exhibit Frenkel defects.

Example,— Yellow colour of ZnS.

**(c) Metal Deficiency due to Cation Vacancies:**

The non stoichiometric compounds may have metal deficiency due to the absence of a metal ion from its lattice site. The charge is balanced by an adjacent ion having higher positive charge. These type of defects are generally shown by compounds of transition metals.

Example, FeS, NiO



## Enhance Your Knowledge

### Electrical Properties of Solid

- Diamagnetic Substance:** These substances are weakly repelled by the magnetic field and do not have any unpaired electron. They act as insulators

$$\uparrow \downarrow, \uparrow \downarrow, \uparrow \downarrow$$

Example,— NaCl, Zn, Cd, Cu<sup>+</sup>, TiO<sub>2</sub>etc.

- Paramagnetic Substances:** These substances are attracted by the magnetic field and have unpaired electrons. They lose magnetism in the absence of magnetic field.

$$\uparrow \downarrow \uparrow \uparrow$$

## 8.20 ■ Solid State

Example, Transition metals like Cr, Mn, Ni, Co, Fe etc. Metal oxides like CuO, VO<sub>2</sub> etc.

- **Ferromagnetic Substances:** These substances are attracted by the magnetic field and show permanent magnetism even in the absence of magnetic field.

Example, Fe, Co, Ni, CrO<sub>2</sub> (used in audio and video tapes) etc.

- This arises due to spontaneous alignment of magnetic momenta in the same direction .

↑↑↑↑↑↑

- Above Curie temperature, there is no ferromagnetism.

- **Antiferromagnetic Substances:** These are the substances which are expected to possess paramagnetism or ferromagnetism on the basis of unpaired electrons but actually have zero net magnetic moment.

Example, MnO, MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, FeO, Fe<sub>2</sub>O<sub>3</sub> etc.

- Anti-ferromagnetism is due to equal number of parallel and antiparallel magnetic momenta which leads to zero resulting magnetic moment.

↑↓↑↓↑↓

- **Ferrimagnetic Substances:** In ferrimagnetic substances, there are unequal number of parallel and antiparallel magnetic momenta which leads to some resulting magnetic moment.

↑↓↓↓↑↓

Example, Fe<sub>3</sub>O<sub>4</sub>, Ferrites

### Effect of Temperature

- The ferromagnetic, anti-ferromagnetic and ferrimagnetic solids change into paramagnetic at a particular temperature.

Example, Ferrimagnetic Fe<sub>3</sub>O<sub>4</sub> on heating to 850 K becomes paramagnetic this is due to alignment of spins in one direction on heating.

### Curie Temperature

Each ferromagnetic substance has a characteristic temperature above which no ferromagnetism is observed this is called curie temperature.

### Piezoelectricity

It is the electricity produced when mechanical stress is applied on polar crystals.

### Pyroelectricity

It is the electricity produced when some polar crystals are heated.

### Ferroelectricity

In some piezoelectric crystals, the dipoles are permanently polarized even in the absence of electric field. However, on applying electric field, the direction of polarization changes. This phenomenon is called ferroelectricity due to analogy with ferromagnetism.

↑↑↑↑↑↑↑

Example, Barium titanate (BaTiO<sub>3</sub>), sodium potassium tartarate (Rochelle salt) and potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>).

### Anti-ferroelectricity

In some crystals, the dipoles align in such a way that they alternately point up and down so that the crystal does not possess any net dipole moment.

↑↓↑↓↑↓

Example, Lead zirconate (PbZrO<sub>3</sub>).

### Superconductivity

Kamerlingh Onnes observed this phenomenon at 4 K in mercury.

A substance is said to be superconducting when it offers no resistance to the flow of electricity. There is no substance which is superconducting at room temperature.

Example, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, Nb<sub>3</sub>Ge alloy, La<sub>1.25</sub>Ba<sub>0.15</sub>CuO<sub>4</sub>, (TMTSF)<sub>2</sub>PF<sub>6</sub> (TMTSF stands for Tetra methyl tetra selena fulvalene) etc.

- Superconductors are widely used in electronic power transmission, building super magnets etc.

**Semi-conductors:** These are electronic conductors having electrical conductivity in the range of 10<sup>4</sup> – 10<sup>7</sup> Ω<sup>-1</sup> cm<sup>-1</sup>.

Example, Si, Ge, Sn (grey only), SiC, Cu<sub>2</sub>O etc.

- Pure substances which are semi conductors are called intrinsic semi conductors Example, Si, Ge.
- If the semi-conductors conductivity is due to impurities they are called extrinsic semi-conductors.
- The addition of impurities to a semi conductor is called doping.

Example, When phosphorous and arsenic (Vth group element) are doped in silica (IVth group element) n-type of conductance is observed.

When IIIrd group element (Ga) is doped p-type of conductance is observed.

**Cohesive Energy:** It is the energy needed to achieve in finitely separated gaseous ions from one mole of anionic crystal lattice that is negative of the Lattice energy.



's'      'g'      'g'

### Bragg's Equation

M. Von Laue told that there is a possibility of diffraction of X-rays by the crystals as the wavelength of X-rays is of nearly same order as the inter-atomic distances in a crystal. Considering this fact Bragg diffracted X-rays by using sodium chloride crystal. He also introduced his equation. This equation gives a simple relationship between the wavelength of X-rays and the distance between the planes in the crystal and the angle of reflection. This equation can be written as:

$$n\lambda = 2d \sin \theta$$

Here

$n$  = Order of reflection; in general it is taken as 1.

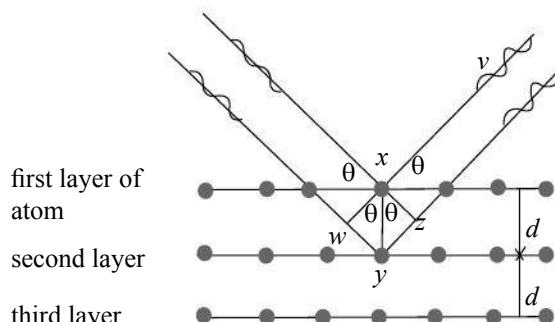
$\lambda$  = Wavelength of X-rays

$d$  = Distance between two layers of the crystals

$\theta$  = Angle of incident light

- As for a given set of lattice planes the value of ' $d$ ' is fixed so the possibility of getting maximum reflection depends only on  $\theta$ . If we increase  $\theta$

gradually a number of positions will be observed at which there will be maximum reflection.



$$\begin{aligned} \text{Path difference} &= WY + YZ \\ &= XY \sin \theta + XY \sin \theta \\ &= 2XY \sin \theta = 2d \sin \theta \end{aligned}$$

The diffraction of two waves of X-rays by the regularly spaced atoms in a crystal.

### Applications

- Bragg's observation has been proved highly beneficial in determining the structures and dimensions of ionic crystalline solids.
- It also helped in describing many properties of X-rays also.
- It helped in the construction of X-ray spectrometer by which the crystalline structure of crystals can be easily described. Example, face centered cubic structure of NaCl.

### Solved Problems from the IITs

- Sodium metal crystallizes in a body centred cubic lattice with the cell edge  $a = 4.29 \text{ \AA}$ . What is the radius of sodium atom?

[IIT 1994]

**Solution** For b.c.c. lattice,

$$\begin{aligned} \text{Radius} &= \frac{\sqrt{3}}{4} \cdot a = \frac{\sqrt{3} \times 4.29}{4} \\ &= 1.8576 \text{ \AA} \end{aligned}$$

- A metallic element crystallizes into a lattice containing a sequence of layers of AB AB AB... any packing of spheres leaves out voids

in the lattice. What percentage by volume of this lattice is empty space?

[IIT 1996]

**Solution** As number of atoms in hcp per unit cell = 6

$$\text{So packing fraction} = \frac{6 \times 4/3 \pi r^3}{\text{Base area} \times C}$$

$$\text{As base area} = 6 \times \frac{\sqrt{3}}{4} \times 4r^2$$

$$\text{or } C = 4r\sqrt{(2/3)}$$

## 8.22 ■ Solid State

Now Packing fraction

$$= \frac{6 \times 4/3 \pi r^3}{6 \times \frac{\sqrt{3}}{4} \times 4 r^2 \times 4r \sqrt{(2/3)}} = 0.74$$

So Void (space) =  $1 - 0.74 = 0.26$

= 29 %

3. Chromium metal crystallizes with a body centered cubic lattice. The length of the unit cell edge is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in g/nm?

[IIT 1997]

**Solution** For b.c.c. lattice,

$$r = \frac{\sqrt{3} \cdot a}{4} = \frac{\sqrt{3} \times 287}{4} = 124.27 \text{ pm}$$

$$d = \frac{M \cdot Z}{N_0 \cdot a^3} = \frac{51.99 \times 2}{6.02 \times 10^{23} \times (287 \times 10^{-10})^3}$$

$$= 7.30 \text{ g/m}^3$$

4. A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride?

[IIT 1997]

**Solution**  $Z = 4$ , M for NaCl = 58.5

$$a = 0.564 \text{ nm} = 0.564 \times 10^{-7} \text{ cm}$$

$$d = \frac{M \cdot Z}{N_0 \cdot a^3} = \frac{58.5 \times 4}{6.02 \times 10^{23} \times (0.564 \times 10^{-7})^3} \\ = 2.16 \text{ g/ml}$$

5. A metal crystallizes into two cubic phases, face centred cubic (f.c.c.) and body centred cubic (b.c.c.) whose unit cell lengths are 3.5 and 3.0 Å, respectively. Calculate the ratio of densities of f.c.c. and b.c.c.

[IIT 1999]

**Solution** Unit cell length (f.c.c.) = 3.5 Å

$$= 3.5 \times 10^{-8} \text{ cm}$$

Unit cell length (b.c.c.) = 3.0 Å

$$= 3.0 \times 10^{-8} \text{ cm}$$

$$d \text{ in f.c.c.} = \frac{M_{Z_1}}{N_0 \times (a_1)^3}$$

$$d \text{ in f.c.c.} = \frac{M_{Z_2}}{N_0 \times (a_2)^3}$$

$$\frac{d_{\text{f.c.c.}}}{d_{\text{b.c.c.}}} = \frac{Z_1}{Z_2} \times \frac{(a_2)^3}{(a_1)^3} = \frac{4 \times (3.0 \times 10^{-8})^3}{2 \times (3.5 \times 10^{-8})^3}$$

$$[Z_1 = 4(\text{f.c.c.}), Z_2 = 2(\text{b.c.c.})]$$

$$= 1.259$$

6. (i) AB crystallizes in a rock salt structure with A : B = 1 : 1. The shortest distance between A and B is  $Y^{1/3}$  nm. The formula mass of AB is 6.023 Y amu where Y is any arbitrary constant. Find the density in kg m<sup>-3</sup>.
- (ii) If measured density is 20 kg m<sup>-3</sup>, identify the type of point defect.

[IIT 2004]

**Solution** (i) As rock salt has fcc structure,  $Z = 4$

$$\text{Now edge length of fcc unit cell} \\ = 2 \times \text{shortest distance between } A^+ \text{ & } B^- \\ = 2 \times Y^{1/3} \text{ nm} = 2 \times Y^{1/3} \times 10^{-9} \text{ m}$$

$$\text{As Density of the crystal} = \frac{Z \times M}{N_0 \times a^3} \\ = \frac{4 \times 6.023 Y}{6.023 \times 10^{23} \times (2 \times Y^{1/3} \times 10^{-9})^3} \\ = 5 \text{ kg/m}^3$$

- (ii) Since there is large difference in theoretically calculated density and actual density, the given solid will have metal excess defect or interstitial defect.

7. In face centred cubic (fcc) crystal lattice, edge length of the unit cell is 400 pm. Find the diameter of the greatest sphere which can be fitted into the interstitial void without distortion of lattice.

[IIT 2005]

**Solution** In fcc unit cell

$$\sigma \sqrt{2} = 4r \\ r = \frac{a \sqrt{2}}{4} = \frac{400 \times \sqrt{2}}{4} \\ = 141.4 \text{ pm.}$$

For octahedral void,

$$2(r + R) = a$$

$$2R = a - 2r$$

$$2R = 400 - 2 \times 141.4$$

$$= 117.16 \text{ pm}$$

So the diameter of greatest sphere = 117.16 pm.

8. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 Å which crystallizes in cubic lattice. If the density is 2 g/cc then find the radius of metal atom. ( $\text{NA} = 6 \times 10^{23}$ ). Give the answer in pm.

[IIT 2006]

### Solution

$$\rho = \frac{ZA}{NV}$$

$$Z = \frac{\rho NV}{A} = \frac{2 \times 6 \times 10^{23} \times (5 \times 10^{-8})^3}{75}$$

$$n = 2$$

$$r = \frac{\sqrt{3}}{4} a = \frac{\sqrt{3}}{4} \times 5 = 2.165 \text{ Å} = 216.5 \text{ pm}$$

The answer may be 216 pm or 217 pm.

## MULTIPLE-CHOICE QUESTIONS

### Straight Objective Type Questions (Single Choice only)

1. The number of octahedral sites per sphere in fcc structure is
 

a. 1	b. 2
c. 3	d. 4
2. The crystal system in which  $a \neq b \neq c$  and the angles  $\alpha \neq \beta \neq \gamma$  is
 

a. cubic	b. hexagonal
c. triclinic	d. monoclinic
3. Number of atoms present in the unit cell of a mono atomic substance of body centered lattice are
 

a. 8	b. 6
c. 4	d. 2
4. In a fcc lattice of anions, the cations occupy the octahedral voids. The coordination number of cations is
 

a. 2	b. 4
c. 6	d. 8
5. Frenkel defect appears in
 

a. ZnS	b. AgI
c. AgBr	d. all of these
6. The number of atoms per unit cell in a simple cubic, face-centered cubic and body centered cubic are ..... respectively.
 

a. 1, 2, 4	b. 1, 4, 2
c. 4, 2, 1	d. 1, 4, 3
7. In a simple cubic cell, an atom at the corner contributes to the unit cell
 

a. 1/2 part	b. 1 part
c. 1/6 part	d. 1/8 part
8. Sodium metal crystallizes in body cubic lattice with cell edge 2.49 Å, the radius of the sodium atom is
 

a. 0.68 Å	b. 1.86 Å
c. 2.86 Å	d. 3.86 Å
9. Presence of small impurities usually makes a metal quite hard because the impurities
 

a. reduce the crystal symmetry	b. reduce the number of slide planes
--------------------------------	--------------------------------------

- c. change the lattice structure of metal
 

d. reduce the number of mobile electrons
------------------------------------------
10. If we mix a pentavalent impurity in a crystal lattice of germanium, what type of semiconductor formation will occur?
 

a. p-type semiconductor	b. n-type semiconductor
c. both of these	d. none of these
11. If the anions (B) form hexagonal closest packing and cations (A) occupy only 2/3 octahedral holes in it, then the general formula of the compound is
 

a. $AB_2$	b. $A_3B_2$
c. $A_2B_3$	d. $A_2B_2$
12. The crystal structure of NaCl is
 

a. bcc	b. fcc
c. scc	d. either (a) or (b)
13. The intermetallic compound LiAg crystallizes in cubic lattice in which both lithium and silver have coordination number of eight. The crystal class is
 

a. simple cube	b. body-centered cube
c. face-centered cube	d. none of these
14. The number of atoms in one unit cell of a face centered cubic lattice is
 

a. 2	b. 4
c. 3	d. 5
15. Close packing is maximum in the crystal lattice of
 

a. body centered	b. simple cubic
c. face centered	d. none of these
16. In crystals of which of the following ionic compounds would you expect maximum distance between centers of cations and anions?
 

a. LiF	b. CsF
c. CsI	d. LiI
17. If three elements A, B and C crystallized in cubic solid lattice with A atoms at corners, B atoms at cube centres and C atoms at the edges, the formula of the compound is
 

a. ABC	b. $A_3B_2C_3$
c. $AB_3C$	d. $ABC_3$

18. The presence of F-centres in a crystal makes it  
 a. conducting      b. non-conducting  
 c. colourless      d. coloured
19. Which of the following statement is correct?  
 a. Silicon doped with Boron is an n-type semiconductor.  
 b. Metals are good conductors of electricity  
 c. Electrical conductivity of semiconductors increases with increasing temperature.  
 d. Both (b) and (c)
20. The range of radius ratio (cationic to anionic) for an octahedral arrangement of ions in an ionic solid is  
 a.  $0.155 - 0.225$       b.  $0 - 0.155$   
 c.  $0.414 - 0.732$       d.  $0.225 - 0.414$
21. In diamond crystal each carbon atom is linked with carbon atoms. The number of carbon atoms linked is  
 a. 2      b. 4  
 c. 3      d. 1
22. In spinel structure, oxides ions are cubical closest packed, whereas  $\frac{1}{8}$ th of tetrahedral holes are occupied by cations  $A^{2+}$  and  $\frac{1}{2}$  of octahedral holes are occupied by cations  $B^{3+}$  ions. The general formula of the compound having spinel structure is  
 a.  $AB_2O_4$       b.  $A_2B_2O_4$   
 c.  $A_2B_6O$       d.  $A_4B_3O$
23. Zn converts its melted state to its solid state, it has HCP structure, then find out nearest neighbours of Zn atom  
 a. 6      b. 8  
 c. 12      d. 4
24. Superconductors are derived from the compounds of  
 a. Lanthanides  
 b. p-block elements  
 c. Transition elements  
 d. Actinides
25. A semiconductor of Ge can be made p-type by adding  
 a. Divalent impurity  
 b. Trivalent impurity  
 c. Tetravalent impurity  
 d. Pentavalent impurity
26. The interionic distance for Cesium chloride crystal will be  
 a.  $\sqrt{3} a/2$       b.  $2 a/\sqrt{3}$   
 c.  $a/2$       d.  $a/2$
27. Which of the following metal oxides is anti-ferromagnetic in nature?  
 a.  $TiO_2$       b.  $MnO_2$   
 c.  $CrO_2$       d.  $VO_2$
28.  $Na_2O$  has anti-fluorite structure. In  $Na_2O$ , the coordination number of  $Na^+$  and  $O^{2-}$  are respectively  
 a. 4, 4      b. 6, 6  
 c. 8, 4      d. 4, 8
29. An  $AB_2$  type of structure is present in  
 a.  $NaCl$       b.  $N_2O$   
 c.  $Al_2O_3$       d.  $CaF_2$
30. The melting point of  $RbBr$  is much lower than that of  $NaF$ , the reason is  
 a. The molar mass of  $NaF$  is smaller than that of  $RbBr$ .  
 b. The two crystals are not isomorphous  
 c. The internuclear distance  $r_c + r_a$  is greater for  $RbBr$  than for  $NaF$   
 d. The bond in  $RbBr$  has more covalent character than the bond in  $NaF$ .
31. Schottky defect defines imperfection in the lattice structure of a  
 a. Gas      b. Plasma  
 c. Liquid      d. Solid
32. Number of atoms in the unit cell of Na (BCC type crystal) and Mg (FCC type crystal) are respectively  
 a. 4, 4      b. 4, 2  
 c. 2, 4      d. 1, 1
33. What is the coordination number of  $Cl^-$  in  $NaCl$  crystal?  
 a. 3      b. 4  
 c. 6      d. 8
34. A particular solid is very hard and has a very high melting point. In solid state it is a non conductor and its melt is a conductor of electricity. Classify the solid.  
 a. Ionic      b. Molecular  
 c. Network      d. Metallic
35. What is the co-ordination number of body centred cube?  
 a. 8      b. 6  
 c. 4      d. 12
36. What is the coordination number of sodium in  $Na_2O$ ?  
 a. 6      b. 4  
 c. 8      d. 2

## 8.26 ■ Solid State

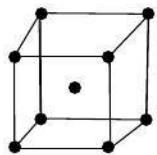
37. Which has no rotation of symmetry?
- Triclinic
  - Cubic
  - Hexagonal
  - Orthorhombic
38. A p-type material is electrically .....
- Neutral
  - Positive
  - Negative
  - Depends upon the concentration of p impurities
  - Depends on the difference of doping impurities and intrinsic impurities
39. In a cubic unit cell, seven of eight corners are occupied by atom A and having of faces are occupied of B. The general formula of the substance having this type structure would be
- $A_7B_{14}$
  - $A_{14}B_7$
  - $A_9B_{24}$
  - $A_9B_{24}$
40. Which of the following shows ferrimagnetism?
- $MnO$
  - $Fe_3O_4$
  - $TiO_2$
  - $CrO_2$
41. In an anti-fluorite structure, cations occupy
- Corners of the cube
  - Tetrahedral voids
  - Centre of the cube
  - Octahedral voids
42. The efficiency of packing is 68 per cent in
- BCC structure
  - FCC structure
  - HCP structure
  - CCP structure
43. In  $AgBr$ , there can occur
- Only Frenkel defect
  - Only Schottky defect
  - Both of these
  - None of these
44. In which of the following pairs, the cations occupy same type of site?
- $CsBr$ ,  $ZnS$
  - $NaCl$ ,  $CsCl$
  - $Na_2O$ ,  $CaF_2$
  - Zinc blende,  $Na_2O$
45. Empty space in ccp lattice is
- 46 %
  - 26 %
  - 64 %
  - 62 %
46. If we know the ionic radius ratio in crystal of ionic solid, what can be known of the following?
- Magnetic property
  - Nature of chemical bond
  - Type of defect
  - Geometrical shape of crystal
47. An example of a face centered cubic lattice is
- Caesium chloride
  - Copper
  - Zinc
  - Sodium
48. A metallic crystal has the BCC type stacking pattern. What percentage of volume of this lattice is empty space?
- 26 %
  - 84 %
  - 32 %
  - 68 %
49. Amorphous substances show
- short and long range order
  - short range order
  - long range order
  - have no sharp m.p.
- (i) and (ii) are correct
  - (ii) and (iv) are correct
  - (ii), (iii) and (iv) are correct
  - (i) and (iv) are correct
50. The fraction of total volume occupied by the atoms present in a simple cube is
- $\pi/6$
  - $\pi/3 \sqrt{2}$
  - $\pi/4 \sqrt{2}$
  - $\pi/4$
51. A compound contains X and Q elements. Atoms Y are in ccp arrangement while X occupy all tetrahedral sites. Formula of compound is:
- $XY$
  - $XY_2$
  - $X_2Y$
  - $X_3Y$
52. With which one of the following elements silicon should be doped so as to give p-type of semi-conductor?
- Phosphorous
  - Boron
  - Germanium
  - Arsenic
53. An ionic compound is expected to have tetrahedral structure if  $r_+/r_-$  lines in the range of
- 0.987 to 12
  - 0.133 to 0.675
  - 1.234 to 0.456
  - 0.225 to 0.414

- 54.** Body centred cubic and face centred unit cells have  $n_1$  and  $n_2$  effective numbers of atoms. Which one of the following ( $n_1$  and  $n_2$ ) combination is correct?
- a. 4.2      b. 2.4  
c. 2.1      d. 1.2
- 55.** Percentage of free space in a body centered cubic unit cell is
- a. 34 %      b. 28 %  
c. 30 %      d. 32 %
- Brainteasers Objective Type Questions  
(Single choice only)**
- 56.** A compound formed by element 'A' and 'B' crystallizes in the cubic structure where 'A' atoms occupy the corners of a cube and 'B' atoms are at the face centres the compound must have the formula:
- a.  $AB_3$       b.  $AB$   
c.  $A_2B$       d.  $A_4B_3$
- 57.** At  $100^\circ\text{C}$  and 1 atm, if the density of liquid water is  $1.0 \text{ gm cm}^{-3}$  and that of water vapour is  $0.0006 \text{ gm cm}^{-3}$ . Then the volume occupied by water molecules in one litre of steam at that temperature is
- a.  $0.6 \text{ cm}^3$       b.  $6.0 \text{ cm}^3$   
c.  $60 \text{ cm}^3$       d.  $0.06 \text{ cm}^3$
- 58.** In the unit cell of an fcc system, the number of octahedral and tetrahedral holes are
- a. 4, 1      b. 1, 8  
c. 4, 8      d. 4, 4
- 59.** The density of solid argon is  $1.65 \text{ g/ml}$  at  $-233^\circ\text{C}$ . If the argon atom is assumed to be sphere of radius  $1.54 \times 10^{-8} \text{ cm}$ , what percentage of solid argon is apparently empty space? (atomic wt. of Ar = 40)
- a. 32%      b. 52%  
c. 72%      d. 62%
- 60.** The second order Bragg diffraction of X-rays with  $\lambda = 1 \text{ \AA}$  from a set of parallel planes in a metal occurs at an angle of  $60^\circ$ . The distance between the scattering planes in the crystal is
- a.  $2.00 \text{ \AA}$       b.  $1.00 \text{ \AA}$   
c.  $0.575 \text{ \AA}$       d.  $1.15 \text{ \AA}$
- 61.** The number of unit cells is  $58.5 \text{ g}$  of NaCl is nearly
- a.  $0.5 \times 10^{23}$       b.  $1.5 \times 10^{23}$   
c.  $3 \times 10^{22}$       d.  $6.0 \times 10^{21}$
- 62.** A solid has a cubic cell with atoms A at the corners, atom B at each face centre and atom C at the body centre. The formula of the solid is
- a. ABC      b.  $AB_3C$   
c.  $A_3B_2C$       d.  $A_8B_6C$
- 63.** Sodium metal crystallizes in body centred cubic lattice with the cell edge,  $4.29 \text{ \AA}$ . The radius of sodium atom is
- a.  $0.85 \text{ \AA}$       b.  $0.185 \text{ \AA}$   
c.  $1.85 \text{ \AA}$       d.  $2.85 \text{ \AA}$
- 64.** An element forms a body centered cubic crystalline substance. The edge length of the unit cell is  $287 \text{ pm}$  and the density of the crystal is  $7.92 \text{ g/cm}^3$ . Calculate the atomic weight of the substance
- a. 56.4 amu      b. 46.4 amu  
c. 36.5 amu      d. 65.4 amu
- 65.** The coordination number of the largest sphere which can be inserted in interstitial voids of an ideal BCC crystal without distorting the lattice would be
- a. 8      b. 6  
c. 4      d. 2
- 66.** In a simple cubic lattice of anions, the side length of the unit cell is  $2.88 \text{ \AA}$ . The diameter of the void in the bond centre is
- a.  $0.461 \text{ \AA}$       b.  $2.108 \text{ \AA}$   
c.  $4.908 \text{ \AA}$       d.  $1.984 \text{ \AA}$
- 67.** A crystal is made of particle A, B & C. A forms FCC packing, B occupies all octahedral voids of A and C occupies all tetrahedral voids of A, if all the particles along one body diagonal are removed then the formula of the crystal would be
- a.  $A_5B_4C_8$       b.  $A_5BC_8$   
c.  $A_8B_4C_5$       d.  $A_5B_2C_8$
- 68.** An alloy of copper, silver and gold is found to have copper constituting the ccp lattice. If silver atoms occupy the edge centres and gold is present at body centre, the alloy will have the formula
- a.  $Cu_4Ag_4Au$       b.  $CuAgAu$   
c.  $Cu_4Ag_3Au$       d.  $Cu_4Ag_2Au$
- 69.** The pyknometric density of sodium chloride crystal is  $2.165 \times 10^3 \text{ kg m}^{-3}$  while its X-ray density is  $2.178 \times 10^3 \text{ kg m}^{-3}$ . The fraction of unoccupied sites in sodium chloride crystal is:
- a.  $5.96 \times 10^{-1}$       b.  $5.96 \times 10^{-3}$   
c. 5.96      d.  $5.96 \times 10^{-2}$

## 8.28 ■ Solid State

70. In the CsCl structure  $r^-/r^+ = 1.37$ . The side length of the unit cell in terms of  $r^-$  is  
 a.  $a = 2r^-$       b.  $a = r^-$   
 c.  $a = 1.414 r^-$       d.  $a = 4r^-$
71. The crystal system of a compound with unit cell dimensions  $a = 0.387$ ,  $b = 0.387$  and  $c = 0.504$  nm and  $\alpha = \beta = 90^\circ$  and  $\gamma = 120^\circ$  is  
 a. Hexagonal  
 b. Cubic  
 c. Rhombohedral  
 d. Orthorhombic
72. Rhodium has a face centered cubic structure and has a density of  $12.4$  g/cm $^3$ . What is its atomic radius?  
 a.  $194$  pm      b.  $234$  pm  
 c.  $314$  pm      d.  $134$  pm
73. If the distance between  $\text{Na}^+$  and  $\text{Cl}^-$  ions in sodium chloride crystal is  $X$  pm, the length of the edge of the unit cell is  
 a.  $X/2$  pm      b.  $2X$  pm  
 c.  $X/4$  pm      d.  $4X$  pm
74. The intercepts made by a plane along the X, Y and Z axes are respectively  $2a$ ,  $2b$  and  $\infty c$  where  $a$ ,  $b$  and  $c$  are the respective unit distances along these axes. The Miller indices of the plane are  
 a.  $0, 2, 2$       b.  $1, 1, 0$   
 c.  $2, 2, \infty$       d.  $1, 1, \infty$
75. The number of tetrahedral voids in the unit cell of a face-centred cubic lattice of similar atoms is  
 a. 6      b. 8  
 c. 10      d. 4
76. A crystalline solid of unknown origin forms an aqueous solution that conducts an electrical current. The solid has a high melting point and shatters when struck with a hammer. The solid is likely to be  
 a. A metallic solid  
 b. A molecular solid  
 c. An ionic solid  
 d. A covalent network solid
77. At very low temperature,  $\text{SO}_2$  crystallizes in a hexagonal lattice. If the cross sectional area of unit cell is  $17.77 \times 10^{-16}$  cm $^2$ , the lattice constant ‘ $b$ ’ is  $7.41$  Å and density is  $0.805$  g/cc then the number of  $\text{SO}_2$  molecules per unit cell is  
 a. 1      b. 2  
 c. 3      d. 4
78. The most unsymmetrical and the most symmetrical crystal systems based on lattice parameters (that is, unit cell lengths and angles), are respectively represented by the examples  
 a. Rhombic sulphur,  $\text{NaCl}$   
 b. Diamond,  $\text{NaCl}$   
 c. Monoclinic sulphur, diamond  
 d.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{NaCl}$
79. What type of crystal defect is indicated in the diagram below?  
 $\text{Na}^+, \text{Cl}^-, \text{Na}^+, \text{Cl}^-, \text{Na}^+, \text{Cl}^-$   
 $\text{Cl}^- \square \text{Cl}^- \text{Na}^+ \square \text{Na}^+$   
 $\text{Na}^- \text{Cl}^- \square \text{Cl}^- \text{Na}^+ \text{Cl}^-$   
 $\text{Cl}^- \text{Na}^+ \text{Cl}^- \text{Na}^+ \square \text{Na}^+$   
 a. Frenkel defect  
 b. Interstitial defect  
 c. Schottky defect  
 d. Frenkel and schottky defects
80. If  $Z$  is the number of atoms in the unit cell that represents the closest packing sequence ...A B C A B C ..., the number of tetrahedral voids in the unit cell is equal to  
 a.  $Z$       b.  $Z/2$   
 c.  $2Z$       d.  $Z/4$
81. In a compound  $\text{PQ}_2\text{O}_4$ , oxide ions are arranged in CCP and cations P are present in octahedral voids. Cations Q are equally distributed among octahedral and tetrahedral voids. The fraction of the octahedral voids occupied is  
 a.  $1/4$       b.  $1/2$   
 c.  $1/3$       d.  $2/3$
82. Assuming the atoms of an element to be hard spheres of radius  $1.00$  Å in c.c.p. or h.c.p. the atomic volume, (being defined as the ratio of atomic weight of the element to its density) calculated per atom is  
 a.  $5.66$  Å $^3$       b.  $6.16$  Å $^3$   
 c.  $1.06$  Å $^3$       d.  $4.18$  Å $^3$
83. In face-centered cubic unit cell, edge length is  
 a.  $2r$       b.  $(\sqrt{3}/2)r$   
 c.  $(4/\sqrt{3})r$       d.  $(4/\sqrt{2})r$
84. A compound alloy of gold and copper crystallizes in a cubic lattice in which the gold atom occupy the lattice points at the corners of a cube and the copper atoms occupy the centers of each of the cube faces. Hence, compound alloy has formula:  
 a.  $\text{Au}_2\text{Cu}$       b.  $\text{AuCu}_3$   
 c.  $\text{AuCu}$       d.  $\text{Au}_3\text{Cu}$

85. A solid  $X^+ Y^-$  has the  $Y^-$  ions arranged as below. If the  $X^+$  ions occupy half of the tetrahedral sites in the structure. The formula of solid is



- a. XY
- b.  $X_2Y$
- c.  $XY_2$
- d.  $X_3Y_4$

86. Then number of nearest neighbours and next near neighbours of a  $Na^+$  ion in a crystal of NaCl are respectively

- a.  $12Cl^-$ ,  $6Na^+$
- b.  $6Cl^-$ ,  $12Na^+$
- c.  $6Cl^-$ ,  $6Na^+$
- d.  $6Na^+$ ,  $12Cl^-$

87. Total volume of atoms present in a face centred cubic unit cell of a metal is ( $r$  is atomic radius)

- a.  $\frac{20}{3} \pi r^3$
- b.  $\frac{24}{3} \pi r^3$
- c.  $\frac{12}{3} \pi r^3$
- d.  $\frac{16}{3} \pi r^3$

88. CsBr crystallizes in a body centered cubic lattice. The unit cell length is 436.6 pm. Given that the atomic mass of Cs = 133 and that of Br = 80 amu and Avogadro number being  $6.02 \times 10^{23}$  mol<sup>-1</sup>, the density of CsBr is

- a. 8.25 g/cm<sup>3</sup>
- b. 4.25 g/cm<sup>3</sup>
- c. 42.5 g/cm<sup>3</sup>
- d. 0.425 g/cm<sup>3</sup>

89. Diamond has face-centred cubic lattice. There are two atoms per lattice point, with the atoms at (000) and (1/4, 1/4, 1/4) coordinates. The ratio of the carbon-carbon bond distance to the edge of the unit cell is

- a. 1/4
- b.  $1/\sqrt{2}$
- c.  $\sqrt{(3/16)}$
- d.  $\sqrt{(1/4)}$

90. A solid has 3 types of atoms namely X, Y and Z. X forms a fcc lattice with Y atoms occupying all the tetrahedral voids and Z atoms occupying half the octahedral voids. The formula of the solid is:

- a. XYZ
- b.  $X_4Y_4Z$
- c.  $X_2Y_4Z$
- d.  $X_4YZ_2$

91. The  $Ca^{+2}$  and  $F^-$  are located in  $CaF_2$  crystal, respectively at face centred cubic lattice points and in
- a. tetrahedral voids
  - b. half of tetrahedral voids
  - c. octahedral voids
  - d. half of octahedral voids

92. The radii of  $Na^+$  and  $Cl^-$  ions are 95 pm and 181 pm respectively. The edge length of NaCl unit cell is

- a. 276 pm
- b. 138 pm
- c. 552 pm
- d. 415 pm

93. An element (with atomic mass = 250 g) crystallizes in a simple cube. If the density of unit cell is 7.2 g cm<sup>-3</sup>, what is the radius of the element?

- a.  $1.93 \times 10^{-6}$  cm
- b.  $1.93 \times 10^{-8}$  cm
- c.  $1.93 \times 10^{-8}$  Å
- d.  $1.93 \times 10^{-8}$  m

94. For hcp packing which of the following will be correct statement?

- (i) Volume of unit cell unoccupied = 68 %
- (ii) Coordination number of HCP = 12
- (iii) This is more efficient packing than ccp
- (iv) It contains both tetrahedral and octahedral voids
- a. (i), (iii)
- b. (ii), (iv)
- c. (i), (iv)
- d. (i), (ii), (iv)

95. A certain metal with density 10.57 gm/ml crystallizes in the f.c.c system. If the number of unit cells per gram  $1.4 \times 10^{21}$ , find the side length of the unit cell.

- a. 4.1 Å
- b. 2.05 Å
- c. 4.25 Å
- d. 6.75 Å

96. For a cubic crystal structure which one the following relations indicating the cell characteristics is correct?

- a.  $a = b = c$  and  $\alpha \neq \beta \neq \gamma \neq 90^\circ$
- b.  $a \neq b \neq c$  and  $\alpha = \beta = \gamma = 90^\circ$
- c.  $a \neq b \neq c$  and  $\alpha \neq \beta$  and  $\gamma \neq 90^\circ$
- d.  $a = b = c$  and  $\alpha = \beta = \gamma = 90^\circ$

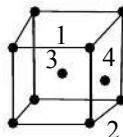
97. The chromium metal exists as a bcc lattice with cell edge 2.88 Å. Its density is 7.20 g/cc. How many atoms does 55 g of chromium contain?

- a.  $32.60/55 N_0$
- b.  $51.77/55 N_0$
- c.  $55/51.77 N_0$
- d.  $55/32.60 N_0$

98. NaCl is doped with  $10^{-4}$  mol % of  $SrCl_2$ , the concentration of cation vacancies will be ( $N_A = 6.02 \times 10^{23}$  mol<sup>-1</sup>)

- a.  $6.02 \times 10^{15}$  mol<sup>-1</sup>
- b.  $6.02 \times 10^{16}$  mol<sup>-1</sup>
- c.  $6.02 \times 10^{17}$  mol<sup>-1</sup>
- d.  $6.02 \times 10^{14}$  mol<sup>-1</sup>

## 8.30 ■ Solid State

- 99.** NaCl is doped with  $2 \times 10^{-3}$  mol % SrCl<sub>2</sub>, the concentration of cation vacancies is
- $12.04 \times 10^{18} \text{ mol}^{-1}$
  - $10.01 \times 10^{18} \text{ mol}^{-1}$
  - $12.04 \times 10^{20} \text{ mol}^{-1}$
  - $4.02 \times 10^{18} \text{ mol}^{-1}$
- 100.** Ag crystallizes as FCC. If radius of Ag is 144 pm then its density will be
- $5 \text{ g cm}^{-3}$
  - $10 \text{ g cm}^{-3}$
  - $6.5 \text{ g cm}^{-3}$
  - $16 \text{ g cm}^{-3}$
- 101.** Iridium crystallizes in a face-centered cubic unit cell that has an edge length at 3.832 Å. The atom in the center of the face is in contact with the corner atoms, as shown in figure. Find the atomic radius of an iridium atom.
- 
- 2.71 Å
  - 0.675 Å
  - 1.916 Å
  - 1.355 Å
- 102.** In the problem and figure given above find the density of iridium metal.
- 11.33 g/cm<sup>3</sup>
  - 2.26 g/cm<sup>3</sup>
  - 22.67 g/cm<sup>3</sup>
  - 21.63 g/cm<sup>3</sup>
- 103.** The cubic unit cell of Al (molar mass 27 g mol<sup>-1</sup>) has an edge length of 4.5 pm. Its density is 2.7 g cm<sup>-3</sup>. The cubic unit cell is
- Edge centred
  - Body centred
  - Face centred
  - Simple
- 104.** In a compound atoms of element Y from ccp lattice and those of element X occupy 2/3<sup>rd</sup> of tetrahedral voids. The formula of the compound will be:
- X<sub>4</sub>Y<sub>3</sub>
  - X<sub>2</sub>Y<sub>3</sub>
  - X<sub>2</sub>Y
  - X<sub>3</sub>Y<sub>4</sub>
- 105.** In an FCC unit cell, atoms are numbered as shown below. The atoms not touching each other are (Atoms numbered 3 is face centre of front face).
- 
- 2 and 4
  - 1 and 2
  - 1 and 3
  - 3 and 4
- 106.** Potassium has a bcc structure with nearest neighbour distance 4.52 Å. Its atomic weight is 39. Its density will be
- 454 kg m<sup>-3</sup>
  - 809 kg m<sup>-3</sup>
  - 1098 kg m<sup>-3</sup>
  - 908 kg m<sup>-3</sup>
- 107.** Percentage of free space in a body centered cubic unit cell is:
- 34 %
  - 28 %
  - 30 %
  - 32 %
- 108.** In AO<sub>2</sub>, the metal ions form a face centred cubic lattice. The oxide ions occupy the tetrahedral sites. The metal ions occupy the faces and corners of the unit cell. the total number of metal ions and oxide ions per unit cell is:
- 2
  - 8
  - 12
  - 4
- 109.** Choose the correct statement from the following:
- Frenkel and Schottky defects are thermodynamic defects.
  - Compounds with Schottky defects do not obey law of constant composition.
  - In compounds with Frenkel defect, among a majority of metal ions of one valency, a few metal ions of another valency are also found.
  - (1) only
  - (2) only
  - (1) and (2)
  - (1), (2) and (3)
- 110.** Br has bcc structure with edge length 4.3 Å. The shortest interionic distance in between Cs<sup>+</sup> and Br<sup>-</sup> is
- 4.3 Å
  - 1.89 Å
  - 3.72 Å
  - 7.32 Å
- 111.** If 'a' stands for the edge length of the cubic systems: simple cubic, body centered cubic and face centered cubic, then the ratio of radii of the spheres in these systems will be respectively,
- $\frac{1}{2} a : \frac{\sqrt{3}}{2} a : \frac{\sqrt{2}}{2} a$
  - $1 a : \sqrt{3} a : \sqrt{2} a$
  - $\frac{1}{2} a : \frac{\sqrt{3}}{4} a : \frac{1}{2\sqrt{2}} a$
  - $\frac{1}{2} a : \sqrt{3} a : \frac{1}{\sqrt{2}} a$
- 112.** G In a CCP lattice of A and B, A atoms are present at the corners while B atoms are at face centres. Then the formula of the compound would be if one of the A atoms from a corner is replaced by C atoms(also monovalent)?

- a.  $A_7B_{24}C_8$   
 b.  $A_7B_{24}C$   
 c.  $A_{24}BC$   
 d.  $AB_{24}C$

113. A solid compound contains X, Y and Z atoms in a cubic lattice with X atoms occupying the corners, Y atoms in the body centered positions and Z atoms at the centers of faces of the unit cell. what is the empirical formula of the compound?

- a. XYZ  
 b.  $XYZ_3$   
 c.  $XY_2Z_3$   
 d.  $X_2Y_2Z_3$

114. KCl crystallizes in the same types of lattice as does NaCl. Given that  $r_{Na^+}/r_{Cl^-} = 0.55$  and  $r_{K^+}/r_{Cl^-} = 0.74$ . Calculate the ratio of the side of the unit cell for KCl to that NaCl.

- a. 1.123  
 b. 0.432  
 c. 1.876  
 d. 1.564

115. A compound is formed by elements A and B. This crystallizes in the cubic structure where the A atoms are at the corners of the cube and B atoms are at the body centers. The simplest formula of the compound is

- a.  $A_6B$   
 b.  $A_8B_4$   
 c. AB  
 d.  $AB_6$

### Multiple Correct Answer Type Questions

116. Titanium monoxide has a rock salt structure. X-ray diffraction data show that the length of one edge of the cubic unit cell for  $TiO$ , where in the ratio of Ti to O is 1 : 1 is  $4.18 \times 10^{-8}$  cm and the density determined by volume and mass measurements is 4.91 g  $cm^{-3}$ . which of the following defects are found
- Schottky defects with cation and anion pair vacancy.
  - Schottky defects with equal number of vacancies on the cation and anion sites.
  - Frenkel defects with cation and anion pair interstitial defects
  - Frenkel defects with equal numbers of interstitials on the cation and anion sites.

117. Packing fraction in an identical solid sphere is 74 % in case of

- bcc structure
- hcp structure
- fcc structure
- simple cubic structure.

118. Select the correct statements here.

- The co-ordination no. of U : O in  $UO_2$  is 8 : 4
- In closest packing of x – atoms, there are  $2x$  tetrahedral holes, and  $x$ – octahedral holes
- In hexagonal packing of oxide ion in Sapphire (the aluminium oxide)  $Al^{3+}$  ions crystallize in  $2/3$  rd of the Octahedral hole, then the formula of Sapphire is  $Al_3O_4$
- If anion B constitutes ccp and all the octahedral voids are occupied by cation (a), the crystal has the same molecular formula AB, if the cation (a) occupies the alternate tetrahedral voids.

119. In anti-fluorite structure

- $r_{Li} + r_{O^{2-}} = \frac{\sqrt{3}a}{4}$
- oxide ions are face centred
- cations are present in all the tetrahedral voids
- cations are face centred and anions are present in all the tetrahedral voids.

120. Which of the following statements are correct?

- halides of all alkali metals and alkaline earth metals have rock salt structure
- cesium halides and beryllium oxides have rock salt structure
- in FCC unit cell, void percentage = 26%
- in zinc blende structure, sulphide ions are face centred and zinc is present in alternate tetrahedral voids

121. Which of the following statements is/are consistent with the properties of a molecular solid?

- A low melting solid
- A compound that conducts electricity when molten
- A solid that is a non-conductor of electricity
- A solid formed by the combination of two non-metallic elements

122. If the radius of  $Na^+$  is 95 pm and that of  $Cl^-$  ion is 181 pm then

- Length of the unit cell is 552 pm
- Length of the unit cell is 380 pm
- Co-ordination no. of  $Na^+$  is 6
- Co-ordination no. of  $Na^+$  is 8

123. Which of the following statements is/are incorrect in the rock-salt structure of an ionic compound?

- Coordination number of cation is six and anion is four.

## 8.32 ■ Solid State

- b. Coordination number of cation is four and anion is six.
- c. Coordination number of each cation and anion is six.
- d. Coordination number of each cation and anion is four.
124. Select the correct statements here.
- a. Hexagonal close packing (hcp) and Cubic close packing (ccp) structure has different co-ordination no.
- b. At high pressure, the coordination number increases
- c. Schottky defect is not shown by CsCl.
- d. Frenkel defect is shown by ZnS.
125. Which of the following statements is/are incorrect in the body centered type centered type cubic structure of an ionic compound?
- a. Coordination number of each cation and anion is eight
- b. Coordination number of each cation and anion is four
- c. Coordination number of each cation and anion is six
- d. Coordination number of each cation and anion is two.
126. In which of the following compounds, cations are present in tetrahedral voids?
- a. ZnS                    b. SrF<sub>2</sub>
- c. NaBr                  d. Na<sub>2</sub>O
127. Select the correct statements in a CsCl crystal.
- a. Cs<sup>+</sup> occupies body centre of Cl<sup>-</sup>
- b. It is impossible for Cl<sup>-</sup> to occupy body centre of Cs<sup>+</sup> because the body centre void of Cs<sup>+</sup> is smaller than Cl<sup>-</sup> ion size
- c. Cs<sup>+</sup> forms a simple cubic lattice, Cl<sup>-</sup> forms a simple cubic lattice
- d. Cl<sup>-</sup> occupies body centre of Cs<sup>+</sup>
128. Which of the following statements for crystals having Schottky defect is/are correct?
- a. Schottky defect are more common in ionic compounds with high co-ordination numbers.
- b. Schottky defect arises due to the absence of a cation or anion from the position which it is expected to occupy.
- c. The density of the crystals having Schottky defect is larger than that of the perfect crystal.
- d. The crystal having Schottky defect is electrical neutral as a whole.
129. Select the correct statements here.
- a. For NaCl unit cell (edge-length = l),  $r_+ + r_- = l/2$
- b. For CsCl unit cell (edge-length = a),  $r_+ + r_- = \sqrt{3}/2 a$
- c. The void space in a b.c.c unit cell is 68%
- d. The void space in a face-centered unit cell is 26 %
130. Which of the following statement for crystals having Frenkel defect is not correct?
- a. Frenkel defects are observed where the difference in sizes of cations and anions is larger.
- b. The density of crystals having Frenkel defect is lesser than that of a pure perfect crystal.
- c. Usually alkali halides do not have Frenkel defect.
- d. In an ionic crystal having Frenkel defect may also contain Schottky defect.
131. In face centred cubic unit cell
- a. face diagonal of the cube which is  $\sqrt{2}a$  is equal to  $4r$
- b. rank of unit cell is 3
- c. effective number of atoms is 4 in FCC
- d. 8 tetrahedral voids per unit cell of FCC
132. Select the correct statements .
- a. Frenkel defect usually shown by ionic compounds having low coordination number.
- b. Stoichiometry of crystal remains unaffected due to Schottky defect.
- c. Density of crystal always increases due to substitutional impurity defect.
- d. F- centres generation is responsible factor for imparting the colour to the crystal.
133. Which of the following does not represent the closest packed arrangement of uniform solid spheres?
- a. simple cubic unit cel
- b. hcp unit cell
- c. face centered cubic unit cell
- d. body centered cubic unit cell
134. Select the incorrect statements.
- a. NaCl changes to CsCl structure on applying pressure.
- b. CsCl changes to NaCl structure on heating.
- c. Co-ordination number increases on heating.
- d. Co-ordination number decreases on applying pressure.

- 135.** Amorphous solids
- have sharp melting points
  - have same physical properties in all directions
  - are super cooled liquids
  - are pseudo solids
- 136.** If we assume 'M' crystallizes in a fcc unit cell and tetrahedral voids are also occupied by 'M' atoms. If the edge of the unit cell is 0.55 nm and the density of 'M' is 2.23 g /cc, which of the following statements are correct?
- 40 % of the tetrahedral voids are occupied by 'M'-atoms in this lattice
  - 50 % of the tetrahedral voids are occupied by 'M'-atoms in this lattice
  - M-M bond length is equal to the sum of radii of 2 'M' atoms which is equal to 0.24 nm.
  - 20% of tetrahedral voids are occupied by 'M'-atoms in this lattice
- 137.** Which of the following statement is/ are correct?
- The co-ordination number of each type of ion in CsCl crystal is 8
  - A metal that crystallizes in bcc structure has a co-ordination no. of 12
  - The length of the unit cell in NaCl is 522 pm ( $r_{\text{Na}}^+ = 95$ ,  $r_{\text{Cl}}^- = 181$  pm)
  - A unit cell of an ionic crystal shares some of its ions with other unit cells
- 138.** Pick out the incorrect statement about CsCl structure.
- CsCl has a bcc structure
  - $\text{Cl}^-$  adopts a simple cubic lattice
  - Coordination no. of both Cs and Cl is 6
  - $\text{Cl}^-$  ions present at cubic sites.
- 139.** Which of the following statements is/are correct?
- The number of carbon atoms in an unit cell of diamond is 4.
  - The number of Bravais lattices in which a crystal can be categorized is 14.
  - The fraction of the total volume occupied by the atoms in a primitive cell is 0.48.
  - Molecular solids are generally volatile.
- 140.** The correct statements (s) regarding defects in solids is/are
- Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion.
  - Frenkel defect is a dislocation defect.

- Trapping of an electron in the lattice leads to the formation of F-center
- Schottky defects have no effect on the physical properties of solids

[IIT 2009]

### Linked-Comprehension Type Questions

#### Comprehension 1

Close-packing of particles results in two highly efficient lattice, hexagonal close- packing (hcp) and cubic close- packed (ccp). In both of these packing 74% space is occupied. The remaining space is present in the form two types of voids that is, octahedral voids and tetrahedral voids.

Packing fraction of a unit cell is defined as the fraction of the total volume of the unit cell occupied by the atom(s) and it can be given as

$$\text{P.F.} = \frac{\text{Volume of the atom(s) present in a unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{Z \times \frac{4}{3} \pi r^3}{a^3}$$

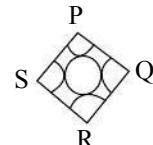
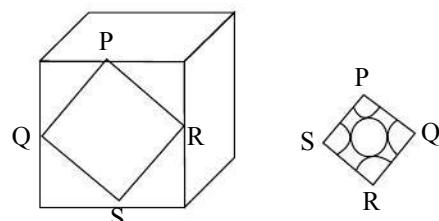
and % of empty space =  $100 - \text{P. F.} \times 100$

here Z = effective number of atoms in a cube

r = radius of an atom

a = edge length of the cube

- 141.** The percentage void spaces per unit volume of unit cell in Zinc floride structure.
- 25.07 %
  - 48%
  - 32 %
  - 74.93 %
- 142.** Consider a cube containing n unit cells of a cubic system. X plane PQRS obtained by joining the mid points of the edge on one of its identical faces had atoms arranged as shown. Let p be the packing fraction. Find the correct choice.



Arrangement of atoms

## 8.34 ■ Solid State

- a.  $n = 1, p = \frac{11}{21}$
- b.  $n = 8, p = \frac{21}{11}$
- c.  $n = 8, p = \frac{11}{21}$
- d.  $n = 1, p = \frac{11}{21\sqrt{2}}$

143. A compound forms hexagonal close-packed structure. What is the total number of voids in 0.6 mol of it?
- a.  $10.8396 \times 10^{22}$
  - b.  $10.8396 \times 10^{23}$
  - c.  $7.2264 \times 10^{23}$
  - d.  $11.2264 \times 10^{23}$

### Comprehension 2

Density of a unit cell can be found out by the relation given below

$$d = \frac{\text{Effective no. of atoms} \times \text{Mass of a unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{Z \cdot M_e}{N_A \cdot a^3}$$

Here, mass of unit cell = mass of effective no. of atoms or ions.

M = At. wt./formula weight .

$N_A$  = Avogadro's no. =  $6.023 \times 10^{23}$

a = edge length of unit cell

144. An unknown metal crystallizes in a body-centered cubic lattice with a unit cell edge length of 5.344 Å. Its density of 0.862 g/cm<sup>3</sup> at 20°C. Identify the metal.

- a. Fe
- b. Cr
- c. K
- d. Na

145. Copper has a specific gravity of 8.93 and crystallizes in a face-centered cubic lattice. Use this information to determine the edge length of the unit cell and the radius of a copper atom.

- a.  $a = 3.52 \text{ \AA}; r = 1.23 \text{ \AA}$
- b.  $a = 3.62 \text{ \AA}; r = 1.28 \text{ \AA}$
- c.  $a = 3.42 \text{ \AA}; r = 1.22 \text{ \AA}$
- d.  $a = 3.82 \text{ \AA}; r = 1.32 \text{ \AA}$

146. Cesium chloride, CsCl, crystallizes in a lattice in which there are chloride ions at each corner of a cube and a cesium ion in a body-centered position.

The edge length, a, is 4.121 Å and the radius of a chloride ion is 1.81 Å. Assuming anion-cation contact along the body diagonal, j, determine the ionic radius of Cs<sup>+</sup>.

- a. 1.66 Å
- b. 1.76 Å
- c. 1.86 Å
- d. 1.57 Å

### Comprehension 3

Atomic radius is half of the distance between nearest neighbouring atoms in a crystal for various types of crystals it can be expressed in terms of edge length of the unit cell. In case of ionic crystals the geometrical shape and coordination number are decided on the bases of radius ratio ( $r_{c+}/r_{a-}$ )

147. Tungsten crystallizes in a body-centered cubic unit cell with an edge length of 317 pm. What is the length (in Pico meters) of a unit cell diagonal that passes through the center atom and the radius of a tungsten atom respectively?

- a. 317 pm, 137 pm
- b. 549 pm, 137 pm.
- c. 549 pm, 274 pm
- d. 317 pm, 274 pm

148. The edge length CsCl unit cell is 412.4 pm. If the ionic radius of Cl<sup>-</sup> ion is 181 pm. Find the ionic radius for Cs<sup>+</sup>:

- a. 173.28 pm
- b. 186.224 pm
- c. 176.148 pm
- d. 231.4 pm

149. Which of the following represent the correct decreasing order of radius ratio?

- a. CsCl > NaCl > ZnS > B<sub>2</sub>O<sub>3</sub>
- b. AgI > BeS > KCl > B<sub>2</sub>O<sub>3</sub>
- c. AgI = BeS > KCl > B<sub>2</sub>O<sub>3</sub>
- d. CsCl > ZnS > NaCl > B<sub>2</sub>O<sub>3</sub>

### Comprehension 4

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagonal and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (HCP), is constituted of a sphere on a flat surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Finally the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be 'r'.

150. The number of atoms in this HCP unit cell is  
 a. 4                      b. 6  
 c. 12                    d. 17

151. The volume of this HCP unit cell is

- a.  $24\sqrt{2}r^3$               b.  $16\sqrt{2}r^3$   
 c.  $12\sqrt{2}r^3$               d.  $\frac{64}{3\sqrt{3}r^3}$

152. The empty space in this HCP unit cell is

- a. 74 %                      b. 47.6 %  
 c. 32 %                      d. 26 %

### Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given. Mark

- (a) if A and R both are correct and R is the correct explanation of A
- (b) if A and R both are correct but R is not the correct explanation of A
- (c) A is true but R is false
- (d) A is false but R is true
- (e) both A and R are false.

153. (A): For fluorite structure, the  $F^-$  ions occupy tetrahedral void, but  $Ca^{+2}$  ions occupy c.c.p.

(R): The radius ratio of fluorite structure is 0.225.

154. (A): Electrical conductivity of semiconductors increases with increasing temperature.

(R): With the increase in temperature, large number of electrons from the valence band can jump to the conduction band.

155. (A): When iodine is heated under atmospheric pressure condition, it transforms to vapour without passing through the liquid state.

(R): If the triple point pressure of a system is high and unless external pressure is applied to exceed the triple point pressure, sublimation will take place.

156. (A): Repulsion energy term for sodium chloride is  $6be^2/n^n$

(R): The term  $6be^2$  is because in case of sodium chloride each sodium ion is surrounded by six chloride ions.

157. (A): In any ionic solid (MX) with Schottky defects, the number of positive and negative ions is the same.

(R): Equal number of cation and anion vacancies are present.

158. (A): Graphite is an example of tetragonal crystal system.

(R): for a tetragonal system,  $a = b \neq c$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$

159. (A): NaCl crystal is sometimes yellow in colour.

(R):  $Na^+$  in the crystal absorbs electron from air and hence gives yellow colour.

160. (A): Anion vacancies in alkali halides are produced by heating the alkali halide crystals with alkali metal vapour

(R): Electrons trapped in anion vacancies are referred to as F-centres.

161. (A): In AgCl crystal, Frenkel defect can be observed.

(R):  $Ag^+$  is a small size cations.

162. (A): In CsCl, the limiting radius ratio should lie in between 0.414 – 0.732.

(R): Coordination numbers of both  $Cs^+$  and  $Cl^-$  ions are 8.

163. (A): Amorphous silica is a photovoltaic substance.

(R): Photovoltaic substance converts sunlight into electricity.

164. (A): Large number of Schottky defect lead to lowering in density of crystal lattice.

(R): The defect is due to missing cation and anion. Equal number of cations and anions are missing to maintain electroneutrality.

165. (A): The substance whose resistance reduces nearly to zero are called superconductors.

(R): Superconductors are diamagnetic substances.

166. (A): The effective number of octahedral voids in CCP structures is 4 per unit cell.

(R): In the CCP structure, there is one octahedral void in the centre of the body and 12 octahedral voids on the 12 edges of the cube and each of these edge based void is shared by four unit cells.

**167. (A):** In close packing of spheres, a tetrahedral void is surrounded by four spheres whereas an octahedral void is surrounded by six spheres

**(R):** A tetrahedral void has a tetrahedral shape whereas an octahedral void has an octahedral shape.

**168. (A):** Group -15 doped crystals of silicon are called a n-type semiconductor.

**(R):** Neutrons are responsible for the semi-conducting properties.

**169. (A):** Group-13 doped crystals of silicon are called a p-type semiconductors.

**(R):** Holes (Positive in charge) appear to be responsible for the semi-conducting properties.

**170. (A):** Band gap in germanium is small because

**(R):** The energy gap of each germanium atomic energy level is infinitesimally small

[IIT 2007]

### Matrix-Match Type Questions

**171.** Match the following:

<b>Column I</b>	<b>Column II</b>
A. Trigonal	(p) $\alpha = \beta = \gamma \neq 90^\circ$
B. Monoclinic	(q) $a = b = c$
C. Rhombic	(r) $a \neq b \neq c$
D. Cubic	(s) $\alpha = \beta = \gamma = 90^\circ$

**172.** Match list-I with list-II and select the correct answer:

<b>List I (shape)</b>	<b>List II (Radius ratio)</b>
A. Planar triangle	(p) 0.732
B. Square planar	(q) 0.225
C. Body centred cubic	(r) 0.115
D. Tetrahedral	(s) 0.414

**173** Match the following:

<b>List I</b>	<b>List II</b>
A. Ferrimagnetic	(p) $\text{Fe}_3\text{O}_4$
b. Ferroelectricity	(q) $\text{BaTiO}_3$
C. Antiferroelectricity	(r) $\text{PbZrO}_3$
D. Diamagnetic	(s) $\text{TiO}_2$
	(t) $\text{KH}_2\text{PO}_4$

**174.** Match the following:

<b>Column I</b>	<b>Column II</b>
A. Fluorite structure	(p) Distance of nearest neighbour $= \frac{\sqrt{3}}{4} a$

B. Zinc blende structure (q) Packing Fraction 73.0 %

C. CsCl structure (r) Packing Fraction 74.0 %

D. Rock salt structure (s) Packing Fraction 79.4 %

**175.** Match the following:

<b>Column I</b>	<b>Column II</b>
A. P-type semi conductor	(p) Electrons are responsible for movement of current
B. N – type semi conductor	(q) Holes are responsible for movement of current
C. Graphite	(r) Doping
D. NaCl	(s) Crystalline

**176.** Match the following:

<b>Column I</b>	<b>Column II</b>
A. Cubic	(p) $a = b = c$
B. Rhombohedral	(q) $a = b \neq c$
C. Tetragonal	(r) $\alpha = \beta = \gamma = 90^\circ$
D. Hexagonal	(s) $\alpha = \beta = 90^\circ \gamma = 120^\circ$
	(t) $\alpha = \beta = \gamma \neq 90^\circ$

**177.** Match the following:

<b>Column I</b>	<b>Column II</b>
A. Diamagnetic	(p) Unpaired electrons
B. Paramagnetic	(q) $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$
C. Ferromagnetic	(r) $\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$
D. Antiferromagnetic	(s) $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$
	(t) $\uparrow\rightarrow\uparrow$

**178.** Match the following:

<b>Column I</b>	<b>Column II</b>
A. If $0.732 \leq x < 1$	(p) Co-ordination no. is 2
B. If $0.414 \leq x < 0.732$	(q) Co-ordination no. is 6
C. If $0.225 \leq x < 0.414$	(r) Co-ordination no. is 4
D. If radius ratio	(s) Co-ordination no. is 8
	$x \left( \frac{r_c}{r_a} \right) < 0.155$

179. Match the following:

Column I	Column II
A. C. No. of $\text{Cs}^+$ and $\text{Cl}^-$ in $\text{CsCl}$ (bcc type) structure	(p) 4, 4
B. C. No. of $\text{Zn}^{2+}$ and $\text{S}^{2-}$ in zinc blende structure	(q) 4, 8
C. C. No. of $\text{Li}^+$ and $\text{O}^{2-}$ in antiflurite structure	(r) 8, 8
D. Co-ordination no. of $\text{Ca}^{2+}$ and $\text{F}^-$ in fluorite structure	(s) 8, 4

180. Match the following:

List I (Crystal system/ Unit cells)	List II (Characteristic features)
A. Simple cubic and face centered cubic	(p) have these cell parameters $a = b = c$ and $\alpha = \beta = \gamma$
B. Cubic and rhombohedral	(q) are two crystal systems
C. Cubic and tetragonal	(r) have only two crystallographic angles of $90^\circ$
D. Hexagonal and monoclinic	(s) belong to same crystal system

[IIT 2007]

### The IIT-JEE Corner

181. A metallic element crystallizes into a lattice containing a sequence of layers of ABABAB..... any packing of spheres leaves out voids in the lattice. What percentage by volume of this lattice is empty space?

- a. 26%
- b. 74%
- c. 50%
- d. 85%

[IIT 1996]

182. Which of the following statement (s) is (are) correct?

- (1) The co-ordination number of each type of ion in  $\text{CsCl}$  crystal is 8.
- (2) A metal that crystallizes in bcc structure has a co-ordination number of 12
- (3) A unit cell of an ionic crystal shares some of its ion with other units cells.
- (4) the length of unit cell in  $\text{NaCl}$  is 552 pm ( $r \text{Na}^+ = 95$  pm,  $r \text{Cl}^- = 181$  pm )

- a. 1, 2
- b. 1, 3
- c. 2, 3
- d. 2, 4

[IIT 1998]

183. The coordination number of a metal crystallizing in a hexagonal close packing structure is

- a. 12
- b. 4
- c. 8
- d. 6

[IIT 1999]

184. In a solid ‘AB’ having  $\text{NaCl}$  structure atoms occupy the corners of the cube unit cell. If all the face centered atoms along one of the axis are removed then the resultant stoichiometry of the solid is

- a.  $\text{AB}_2$
- b.  $\text{A}_2\text{B}$
- c.  $\text{A}_4\text{B}_3$
- d.  $\text{A}_3\text{B}_4$

[IIT 2001]

185. A substance  $\text{AxBy}$  crystallizes in a face centered cubic (FCC) lattice in which atoms ‘A’ occupy each corner of the cube and atoms ‘B’ occupy the centers of each face of the cube. Identify the correct composition of the substance  $\text{AxBy}$ .

- a.  $\text{AB}_3$
- b.  $\text{A}_4\text{B}_3$
- c.  $\text{A}_3\text{B}$
- d. Composition cannot be specified

[IIT 2002]

186. When the temperature is increased, surface tension of water

- a. increases
- b. decreases
- c. remains constant
- d. shows irregular behaviour

[IIT 2002]

187. The compound in which cation occupy alternate tetrahedral voids in cubic closed packing (CCP)

- a.  $\text{NaCl}$
- b.  $\text{ZnS}$
- c.  $\text{Na}_2\text{O}$
- d.  $\text{CaF}_2$

[IIT 2005]

188. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 Å which crystallizes in cubic lattice. If the density is 2 g/cc then find the radius of metal atom. ( $\text{NA} = 6 \times 10^{23}$ ). Give the answer in pm.

- a. 217
- b. 215
- c. 107
- d. 434

[IIT 2006]

189. The coordination number of Al in the crystalline state of  $\text{AlCl}_3$  is

- a. 3
- b. 6
- c. 4
- d. 8

[IIT 2009]

**ANSWERS****Straight Objective Type Questions**

- |       |       |       |       |       |       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1. a  | 2. c  | 3. d  | 4. c  | 5. d  | 6. b  | 7. d  | 8. b  | 9. b  | 10. b | 11. c | 12. b |
| 13. b | 14. b | 15. c | 16. c | 17. d | 18. d | 19. d | 20. c | 21. d | 22. a | 23. c | 24. b |
| 25. b | 26. a | 27. c | 28. d | 29. d | 30. c | 31. d | 32. c | 33. c | 34. a | 35. a | 36. b |
| 37. a | 38. a | 39. c | 40. b | 41. b | 42. a | 43. c | 44. d | 45. b | 46. d | 47. b | 48. c |
| 49. b | 50. a | 51. c | 52. b | 53. d | 54. b | 55. d |       |       |       |       |       |

**Brainteasers Objective Type Questions**

- |        |        |        |        |        |        |        |        |        |        |        |        |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 56. a  | 57. a  | 58. c  | 59. d  | 60. d  | 61. b  | 62. b  | 63. c  | 64. a  | 65. d  | 66. b  | 67. a  |
| 68. c  | 69. b  | 70. a  | 71. a  | 72. d  | 73. b  | 74. b  | 75. b  | 76. c  | 77. a  | 78. d  | 79. c  |
| 80. c  | 81. b  | 82. a  | 83. d  | 84. b  | 85. b  | 86. b  | 87. d  | 88. a  | 89. c  | 90. c  | 91. a  |
| 92. c  | 93. b  | 94. b  | 95. a  | 96. d  | 97. c  | 98. c  | 99. a  | 100. b | 101. d | 102. c | 103. c |
| 104. a | 105. b | 106. d | 107. d | 108. c | 109. a | 110. c | 111. c | 112. b | 113. b | 114. a | 115. c |

**Multiple Correct Answer Type Questions**

- |              |              |              |              |              |              |              |
|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| 116. a, b    | 117. b, c    | 118. a, b, d | 119. a, b, c | 120. c, d    | 121. a, c, d | 122. a, c    |
| 123. a, b, d | 124. a, b, d | 125. a, c, d | 126. a, d    | 127. a, c, d | 128. a, b, d | 129. a, b, d |
| 130. a, c, d | 131. c, d    | 132. a, b, d | 133. a, d    | 134. c, d    | 135. b, c, d | 136. b, c    |
| 137. a, c, d | 138. c, d    | 139. a, b, d | 140. b, c    |              |              |              |

**Linked-Comprehension Type Questions****Comprehension 1**

141. a      142. c      143. b

**Comprehension 2**

144. c      145. b      146. b

**Comprehension 3**

147. b      148. c      149. a

**Comprehension 4**

150. b      151. a      152. d

**Assertion Reason Type Questions**

- |        |        |        |        |
|--------|--------|--------|--------|
| 153. c | 154. a | 155. a | 156. a |
| 157. a | 158. e | 159. c | 160. b |
| 161. a | 162. d | 163. b | 164. a |
| 165. b | 166. a | 167. c | 168. c |
| 169. a | 170. b |        |        |

### Matrix-Match Type Questions

171. A - (p, q), B - (r), C - (r, s), D - (q, s)
172. A - (r), B - (s), C - (p), D - (q)
173. A-(p), B-(q, t), C-(r), D-(s)
174. A - (p, s), B - (p, r), C- (q), D - (s)
175. A - (q, r), B - (r, p), C - (p, s), D - (s)
176. A - (p, r,), B - (p, t), C - (q, r), D - (q, s)
177. A - (q), B - (p, t), C - (p, r), D - (p, s)
178. A -(s), B - (q, r), C - (r), D - (p)
179. A - (r), B - (p), C - (q), D - (s)
180. A -( p, s), B -( p, q), C -(q), D - (q, r )

### The IIT-JEE Corner

181. a      182. b      183. a      184. c      185. a      186. b      187. b      188. a      189. b

### Hints and Explanations

#### Straight Objective Type Questions

- As number of octahedral sites = number of ions in the packing  
So number of octahedral sites per sphere = 1.
- A body centered lattice has 8 atoms.  
Contribution of a particle at the corner =  $1/8$ .  
The number of atoms to be assigned to unit cell  
 $= 8 \times 1/8 = 1$   
Contribution of a particle at the body centre = 1.  
So total number of atoms present in the unit cell  
 $= 1 + 1 = 2$ .
- Body diagonal =  $4 \times r(\text{Na}) = \sqrt{3} \times a$   
 $4 \times r(\text{Na}) = \sqrt{3} \times 4.29$   
 $r(\text{Na}) = \frac{\sqrt{3}}{4} \times 4.29 = 1.86 \text{ \AA}$
- NaCl crystal has fcc (face centered cubic) structure because in NaCl the  $\text{Na}^+$  atom occupy all the eight corners of the cube,  $\text{Cl}^-$  ions are present at all the corners and at the centre of each face of the cube.
- The maximum proportion of volume filled or maximum packing by hard spheres in simple cubic body centered and face centered cubic system are 0.52, 0.68 and 0.74 respectively.
- $A : B : C = (8 \times 1/8) : (1 \times 1) : (6 \times 1/2)$   
 $= 1 : 1 : 3$   
So the formula is  $\text{ABC}_3$ .
- In diamond crystal each carbon atom is linked to four other carbon atoms by strong covalent bonds in a tetrahedral manner.
- HCP is a closed packed arrangement in which the unit cell is hexagonal and co-ordination number is 12.
- Ge is group 14 element. Positive holes can be created by adding group 13 element i.e. trivalent impurity.
- Anti-fluorite structures like  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Rb}_2\text{O}$ ,  $\text{Rb}_2\text{S}$ ,  $\text{Na}_2\text{S}$  possess 4 : 8 coordination
- $\text{AB}_2$  type of structure is present in  $\text{CaF}_2$  as,  
$$\text{AB}_2 \rightleftharpoons \text{A}^{2+} + 2\text{B}^-$$
  
$$\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-$$
- Schottky defect defines imperfection in the lattice structure of a solid in which cation and anion are missing in equal numbers from their lattices.
- In  $\text{Na}_2\text{O}$  each  $\text{O}^{2-}$  ion is surrounded by 8 sodium ions and each sodium ion is surrounded by 4  $\text{O}^{2-}$  ions. Hence the coordination number of sodium is 4.

## 8.40 ■ Solid State

39.  $A : B = 7/8 : 3 = 7 : 24$

So the formula is  $A_7B_{24}$ .

41. In antifluorite structure, oxide ions are present in FCC packing and metal ions occupy all the tetrahedral voids.

43. AgBr has both Schottky and Frenkel defects.

44. In ZnS and  $Na_2O$ , the coordination number (4 : 4) and (4 : 8) respectively.  $Zn^{2+}$  and  $Na^+$  possess same coordination number and occupy the same sites that is tetrahedral sites.

46. In ionic crystals, the coordination numbers as well as the geometrical shapes of the crystals depend mainly on the relative sizes of the ions. The ratio of the positive and negative ions is called radius ratio.

47. Zn is HCP, Na and  $CsCl$  are BCC while Cu is CCP or FCC.

48. In BCC, 68 % space is occupied and remaining 32 % is empty.

50. In simple cubic arrangement it is  $\pi/6$  or 0.52.

52. If silicon is doped with any of the element of group III (B, Al, Ga etc.) of the periodic table, p-type of semiconductor will be obtained.

53.  $r^+ = 0.225$  to 0.414 for ionic compound

$r^-$  having tetrahedral structure

55. For body centered cubic structure

Packing fraction = 0.68 that is, 68 % of the unit cell is occupied by atoms and 32 % is empty.

### Brainteasers Objective Type Questions

56. If atoms 'A' occupy corners then total number of atom 'A' in a crystal

$$= 1/8 \times 8 = 1$$

Now atoms 'B' occupy face centres thus number of atom 'B' =  $1/2 \times 6 = 3$

Therefore, formula of compound is  $AB_3$

57. Mass of water molecules in 1 lit of steam

$$= 1000 \text{ cm}^3 \times 0.0006 \text{ gm cm}^{-3}$$

$$= 0.6 \text{ gm}$$

Volume occupied by water molecules in steam

$$= \frac{\text{Mass of water}}{\text{Density of water}} = \frac{0.6 \text{ gm}}{1.0 \text{ gm/cm}^3}$$

$$= 0.6 \text{ cm}^3$$

58. In an fcc system, number of atoms in the unit cell is, at the corners  $8 \times 1/8 = 1$

at the face centers  $6 \times 1/2 = 3$

Total = 4

For each atom there is one octahedral void and two tetrahedral voids

59. As volume of one atom of Ar =  $\frac{4}{3} \pi r^3$

Number of atoms in 1.65 g or one mL

$$= \frac{1.65}{40} \times 6.023 \times 10^{23}$$

So total volume of all atoms of Ar in solid state

$$= \frac{4}{3} \pi r^3 \times \frac{1.65}{40} \times 6.023 \times 10^{23}$$

$$= \frac{4}{3} \times \frac{22}{7} \times (1.54 \times 10^{-8})^3 \times \frac{1.65}{40}$$

$$\times 6.023 \times 10^{23}$$

$$= 0.380 \text{ cm}^3$$

Volume of solid argon = 1  $\text{cm}^3$

Hence % of empty space

$$= \frac{[1 - 0.380]}{1} \times 100$$

$$= 62 \%$$

60.  $n\lambda = 2d \sin \theta$

$$2 \times 1 = 2 \times d \sin \theta$$

$$2 = 2d \frac{\sqrt{3}}{2} \quad (\sin 60^\circ = \sqrt{3}/2)$$

$$d = 2/\sqrt{3} = 1.15 \text{ \AA}$$

61. 58.5 g  $NaCl$  = 1 mole

$$= 6.02 \times 10^{23} \text{ NaCl units}$$

One unit cell contains 4  $NaCl$  units.

Hence number of unit cells present in 58.5 g  $NaCl$

$$= \frac{6.02 \times 10^{23}}{4} = 1.5 \times 10^{23}$$

62. Number of atom A,  $1/8 \times 8 = 1$

Number of atom B,  $1/2 \times 6 = 3$

Number of atom at the body center C,

$$1 \times 1 = 1$$

Formula is  $AB_3C$

63. Cell edge = 4.29 Å, r = ?

$$\begin{aligned} r &= \frac{\sqrt{3}}{4} a = \frac{\sqrt{3}}{4} \times 4.29 \\ &= \frac{1.732 \times 4.29}{4} = 1.85 \text{ Å} \end{aligned}$$

66. Body diagonal of cubic lattice =  $a\sqrt{3}$

Diameter of the void in the body center  
 $= a\sqrt{3} - a$   
 $= (1.732 \times 2.88) - 2.88$   
 $= 4.988 - 2.88 = 2.108 \text{ Å}$

67. On removing all particles along one body diagonal are removed then 2A particles from corners, 1B particles and 2C particles are removed this means the no. of particles atoms are as follows

No .of A- particles =  $6 \times 1/8 + 6 \times 1/2$   
 $= \frac{15}{4}$

No. of B – particles = 6

No. of C – particles = 3

So the formula is  $A_{15/4} B_6 C_3$   
i.e.  $A_5 B_4 C_8$

68. According to question Au is at the body centre so Au = 1

Ag is at the edge centre =  $12 \times 1/4 = 3$

Cu is having ccp lattice

Cu atoms =  $8 \times 1/8 + 6 \times 1/2$   
 $= 1 + 3 = 4$

So the formula is  $Cu_4 Ag_3 Au$

69. d (pyknometric) = d (observed)

$= 2.165 \times 10^3 \text{ kg/m}^3$

d (X-ray) = d (calculated)

$= 2.178 \times 10^3 \text{ kg/m}^3$

So density decrease

$= (2.178 \times 10^3 - 2.165 \times 10^3)$

$= 0.013 \times 10^3 \text{ kg/m}^3$

$= 13 \text{ kg/m}^3$

Hence fraction of un-occupied sites

$= \frac{\text{density decrease}}{\text{d(calculated)}}$

$$= \frac{13}{2.178 \times 10^3} = 5.96 \times 10^{-3}$$

So the fraction of unoccupied site in sodium chloride crystal is  $5.96 \times 10^{-3}$ .

70. Body diagonal =  $2(r^+ + r^-) = \sqrt{3} a$

$$2(r^- + 1.37 + r^-) = 1.732 a$$

$$2(0.732 r^- + r^-) = 1.732 a$$

$$2 r^- = a.$$

71. For the given crystal,

$$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$$

These are the characteristic of a hexagonal system.

74. Reciprocal of intercepts:

$$\frac{1}{2}, \frac{1}{2}, \frac{1}{\infty}$$

So integral numbers : 1 1 0.

75. A face centered cubic lattice has 4 atoms per unit cell in the packing. Number of tetrahedral voids is double the number of atoms in the packing that is 8.

77. Volume of unit cell = Area × b

$$= 17.77 \times 10^{-16} \times 7.41 \times 10^{-8}$$

$$= 131.68 \times 10^{-24} \text{ cc}$$

$$\text{Mass of unit cell} = V \times d$$

$$= 131.68 \times 10^{-24} \times 0.805$$

$$= 106 \times 10^{-24} \text{ g}$$

number of  $\text{SO}_2$  molecule per unit cell

$$= \frac{106 \times 10^{-24}}{64} \times 6.023 \times 10^{23} = 1$$

78. Most symmetric crystal system:

Cubic :  $a = b = c$  and  $\alpha = \beta = \gamma = 90^\circ$

Example, NaCl, diamond

Most unsymmetric system:

triclinic:  $a \neq b \neq c$  and  $\alpha \neq \beta \neq \gamma \neq 90^\circ$

example.,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

monoclinic:  $a \neq b \neq c$  and  $\alpha = \beta = 90^\circ, \gamma \neq 90^\circ$

example., monoclinic sulphur

79. When equal number of cations and anions (such that charges are equal) are missing ( $1 \text{ Na}^+, 1 \text{ Cl}^-/1 \text{ Fe}^{2+}, 2\text{Cl}^-$ ).

It is a case of Schottky defect.

## 8.42 ■ Solid State

- 80.** Number of tetrahedral voids in a unit cell  
 $= 2 \times \text{number of sphere in unit cell}$   
 $= 2Z$
- 81.** Number of oxide ions = 4  
 Number of octahedral voids = 4  
 Number of Tetrahedral voids = 8  
 $\text{Fraction} = \frac{(1/X) + (1/Y)}{4} = \frac{2}{4} = \frac{1}{2}$ .
- 82.** Size (volume) of the sphere  $4/3 \pi r^3$   
 $= 4/3 \pi \times 1^3 \text{ \AA}^3$ .  
 The void in c.c.p. and h.c.p. = 26 %.  
 So the required atomic volume  
 $= \frac{4}{3} \times \pi \times \frac{100}{74} \text{ \AA}^3 = 5.66 \text{ \AA}^3$
- 83.** In FCC structure,  
 $r = \frac{a}{2\sqrt{2}}$  or  $a = 2\sqrt{2}r$   
 $= 2\sqrt{2}r \times \frac{\sqrt{2}}{\sqrt{2}} = \frac{4}{\sqrt{2}}r$ .
- 84.** Number of Au atoms at the corners =  $8/8 = 1$   
 Number of Cu atoms at the faces =  $6/2 = 3$   
 So formula of the compound =  $\text{AuCu}_3$ .
- 85.** Number of  $\text{Y}^-$  ions in unit cell =  $8 \times 1/8 + 1 = 2$   
 Number of  $\text{X}^+$  ions in unit cell = 4  
 So the formula is  $\text{X}_2\text{Y}$ .
- 86.** NaCl crystal has face-centered lattices in  $\text{Na}^+$  and  $\text{Cl}^-$  ions, interpenetrating. The co-ordination number of  $\text{Na}^+$  is 6, that is, each  $\text{Na}^+$  ion is immediately surrounded by 6  $\text{Cl}^-$  ions (similarly each  $\text{Cl}^-$  ion is immediately surrounded by 6  $\text{Na}^+$  ions) and the next nearest neighbour of  $\text{Na}^+$  is 12  $\text{Na}^+$  ions.
- 87.** Volume of atoms in cell =  $\frac{4}{3} \pi r^3 \times n$   
 $(n = 4 \text{ for fcc})$   
 $= \frac{4}{3} \times \pi r^3 \times 4 = \frac{16}{3} \pi r^3$
- 88.** Density =  $\frac{Z \times M}{a^3 \times N_0}$ .  
 For BCC,  $Z = 2$ ,  $M_{\text{CsBr}} = 213$
- 90.**  $\frac{2 \times 213}{(4.366 \times 10^{-8})^3 \times 6.023 \times 10^{-23}} = 8.250 \text{ g/cm}^3$ .  
 $X (\text{fcc}) = 8 \times 1/8 = 1$  that is 1  
 $Y (\text{tetrahedral voids}) = 2$  that is 2  
 $2 (\text{octahedral voids}) = 1$  that is  $1/2$   
 $X : Y : 2$   
 $1 : 2 : 1/2$   
 $2 : 4 : 1$   
 So formula =  $\text{X}_2\text{Y}_4\text{Z}$
- 91.** In  $\text{CaF}_2$  crystal, the  $\text{Ca}^{2+}$  ions are present at all corners and at the centre of each face of the cube and the  $\text{F}^-$  ions occupy all the tetrahedral sites.
- 95.** density = 10.57 gm/ml  
 $\text{Volume/gram} = \frac{1}{10.57} \text{ ml/gm}$   
 As this contains  $1.4 \times 10^{21}$  unit cells, so the volume of 1 unit cell  
 $= \frac{1}{10.57 \times 1.4 \times 10^{21}} \text{ ml}$   
 that is,  $\frac{10^{24}}{10.57 \times 1.4 \times 10^{21}} (\text{\AA})^3$   
 $= 67.5 (\text{\AA})^3$   
 Hence side length =  $(67.5)^{1/3} \text{\AA} = 4.1 \text{\AA}$
- 98.** As each  $\text{Sr}^{2+}$  ion introduces one cation vacancy, therefore, concentration of cation vacancies = mole % of  $\text{SrCl}_2$  added.  
 So concentration of cation vacancies  
 $= 10^{-4} \text{ mole \%}$   
 $= \frac{10^{-4}}{100} \times 6.023 \times 10^{23}$   
 $= 6.023 \times 10^{23} \times 10^{-6} = 6.023 \times 10^{17}$
- 99.** For each  $\text{Sr}^{2+}$  added, one cationic vacancy is created, because two  $\text{Na}^+$  ions are removed.  
 Number of cation vacancy =  $2 \times 10^{-3}$  mole % of  $\text{NaCl}$   
 $= \frac{2 \times 10^{-3}}{100} \text{ mol}^{-1} \text{ of NaCl}$   
 $= 2 \times 10^{-5} \times 6.02 \times 10^{23} \text{ mol}^{-1} \text{ of NaCl}$

$= 12.04 \times 10^{18} \text{ mol}^{-1}$  of NaCl

$$\begin{aligned} 101. \quad r &= \frac{\sqrt{2} \cdot a}{4} \\ &= \frac{\sqrt{2} \times 3.832}{4} \\ &= 1.355 \text{ \AA} \end{aligned}$$

$$\begin{aligned} 102. \quad d &= \frac{Z \times M}{(a)^3 \times N_0} \\ &= \frac{4}{(3.832 \times 10^{-8} \text{ cm})^3} \times \frac{192.22 \text{ g}}{6.022 \times 10^{23}} \\ &= 22.67 \text{ g/cm}^3 \end{aligned}$$

104. Number of atoms of Y = 4

$$\text{Number of atoms of X} = \frac{2}{3} \times 8$$

Hence, the formula of compound is  $X_4Y_3$ .

105. As atoms along one edge or at corners don't touch each other in fcc cell.

107. For body centered cubic structure

Packing fraction = 0.68 that is, 68 % of the unit cell is occupied by atoms and 32 % is empty.

108.  $A^{4+}$  ions =  $6 \times \frac{1}{2} + 8 \times \frac{1}{2} = 4$

$$O^{2-} \text{ ions} = \frac{2O^{2-}}{1A^{4+}} \times 4A^{4+} = 8$$

111. For simple cubic:

$$r^+/r^- = \frac{a}{2}.$$

Here a = edge length &  $r^+/r^-$  = interatomic distance

For body centered:

$$r^+/r^- = \frac{a\sqrt{3}}{4}$$

For face centered:

$$r^+ + r^- = \frac{a}{2\sqrt{2}}$$

Therefore ratio of radii of the three will be

$$\frac{a}{2} : \frac{a\sqrt{3}}{4} : \frac{a}{2\sqrt{2}}$$

112. No. of A atoms =  $7 \times 1/8$

$$= \frac{7}{8}$$

No. of B atoms =  $\frac{1}{2} \times 6 = 3$

No. of C atoms = 1/8

So the formula is  $A_{7/8} B_3 C_{1/8}$

i.e.  $A_7 B_{24} C$

113. Atoms of X per unit cell =  $8 \times \frac{1}{8} = 1$   
Atoms of Y per unit cell = 1  
Atoms of Z per unit cell =  $6 \times \frac{1}{2} = 3$   
Hence the formula is  $XYZ_3$ ,

$$114. \frac{r_{Na}^{\pm}}{r_{Cl}^{-}} = 0.55 \quad \text{and} \quad \frac{r_K^{\pm}}{r_{Cl}^{-}} = 0.74$$

$$\frac{r_{Na}^{\pm}}{r_{Cl}^{-}} + 1 = 0.55 + 1 \quad \text{and} \quad \frac{r_K^{\pm}}{r_{Cl}^{-}} = 0.74 + 1$$

$$\frac{r_{Na}^{\pm} + r_{Cl}^{\pm}}{r_{Cl}^{-}} = 1.55 \quad \text{and} \quad \frac{r_K^{\pm} + r_{Cl}^{\pm}}{r_{Cl}^{-}} = 1.74$$

Now edge length ratio of KCl and NaCl is

$$\frac{1.74}{1.55} = \frac{r_K^{\pm} + r_{Cl}^{\pm}}{r_{Cl}^{-}} \times \frac{r_{Cl}^{-}}{r_{Na}^{\pm} + r_{Cl}^{\pm}} = 1.22$$

115. AB compound crystallizes in the cubic structure.

A atoms are at the corners of the cube.

So, No. of A atoms per unit cell

$$= 8 \times 1/8 = 1.$$

No. of B atoms per unit cell = AB

As, Simplest formula of the compound = AB.

### Multiple Correct Answer Type Questions

139. Packing fraction for a cubic unit cell is

$$f = \frac{z \times 4}{3 \pi r^3/d^3}$$

Here a = Edge length, r = radius of cation and anion

Efficiency of packing in simple cubic or primitive cell =  $\pi/6 = 0.52$

that is, 52 % of unit cell is occupied by atoms and 48 % is empty. It means it is incorrect.

141. As there are four anions and 8 tetrahedral holes per unit cell, so the fraction of volume occupied by spheres/unit cell volume of the unit cell can be given as:

$$= \frac{4 \times (4/3 \pi r^3 a) + 1/2 \times 8 \times (4/3 \pi r^3 c)}{16 \sqrt{2} r^3 a}$$

## 8.44 ■ Solid State

$$= \frac{\pi}{3\sqrt{2}} \left\{ 1 + \left( \frac{r_c}{r_a} \right)^3 \right\}$$

As for tetrahedral holes,

$$\frac{r_c}{r_a} = 0.225 = \frac{\pi}{3\sqrt{2}} \{ 1 + (0.225)^3 \}$$

$$= 0.7493$$

So void volume =  $1 - 0.7493$

= 0.2507/unit cell volume of unit cell per cent void space = 25.07 %

- 143.** No. of atoms in the close packing = 0.6 mol

$$= 0.5 \times 6.022 \times 10^{23} = 3.6132 \times 10^{23}$$

No. of octahedral voids = No. of atoms in the packing =  $3.6132 \times 10^{23}$

No. of tetrahedral voids =  $2 \times$  No. of atoms in the packing

$$= 2 \times 3.6132 \times 10^{23} = 7.2264 \times 10^{23}$$

Total no. of voids =  $3.6132 \times 10^{23} + 7.2264 \times 10^{23}$

$$= 10.8396 \times 10^{23}$$

- 146.** Body diagonal =  $a\sqrt{3} = 4.121 \text{ \AA} \sqrt{3}$

$$= 4.121 \text{ \AA} (1.732) = 7.138 \text{ \AA}$$

$$2r_{Cs}^+ + 2r_{Cl}^- = 7.138 \text{ \AA}$$

$$\text{So } 2r_{Cs}^+ = 7.138 \text{ \AA} - 2r_{Cl}^-$$

$$= 7.138 \text{ \AA} - 2(1.81 \text{ \AA})$$

$$2r_{Cs}^+ = 3.52 \text{ \AA}, \text{ each Cs}^+ \text{ radius} = \frac{3.52 \text{ \AA}}{2}$$

$$= 1.76 \text{ \AA}$$

- 147.** W is body - centered cubic. d = 317 pm

a = edge = d; b = face diagonal; c = body diagonal

$$b^2 = 2a^2$$

$$c^2 = a^2 + b^2$$

$$c^2 = a^2 + 2a^2 = 3a^2$$

$$c = \sqrt{3} a$$

$$\text{unit cell body diagonal} = \sqrt{3} d = \sqrt{3} (317) = 549 \text{ pm}$$

$$\begin{aligned} r &= \frac{d}{4} \\ &= \frac{549}{4} \\ &= 137 \text{ pm} \end{aligned}$$

- 148.** Body diagonal =  $\sqrt{3} d = \sqrt{3} (412.4) = 714.297 \text{ pm}$

$$\begin{aligned} \text{Cs - Cl bond} &= \text{body diagonal}/2 = (714.297)/2 \\ &= 357.1 \text{ pm} \end{aligned}$$

$$\text{Cs - Cl bond length} = r_{Cs}^+ + r_{Cl}^-$$

$$357.148 = r_{Cs}^+ + r_{Cl}^-$$

$$357.148 = r_{Cs}^+ + 181 \text{ pm}$$

$$r_{Cs}^+ = 357.148 - 181$$

$$= 176.148 \text{ pm}$$

- 150.** Total no. of atoms in 1 unit cell

$$= (12 \times 1/6) + 3 + (2 \times 1/2) = 6$$

- 151.** Height of unit cell =  $4r\sqrt{2/3}$

$$\text{Base area} = 6 \times \sqrt{3}/4 (2r)^2$$

$$\text{volume} = \text{height} \times \text{base area}$$

$$= 4r\sqrt{2/3} \times 6 \times \sqrt{3}/4 (2r)^2 = 24\sqrt{2}r^3$$

- 152.** Packing fraction =

$$\frac{\text{volume of the atoms in one unit cell}}{\text{volume of one unit cell}}$$

$$= \frac{6 \times 4}{3 \pi r^3 / 24\sqrt{2}r^3}$$

$$= \frac{\pi}{3\sqrt{2}}$$

$$= 0.74 = 74 \%$$

$$\text{Packing fraction} = 74\%$$

$$\text{Empty space} = 26\%$$

### The IIT-JEE Corner

- 181.** Number of atoms in hcp is 6 per unit cell.

$$\text{Packing fraction} = \frac{6 \times 4}{3 \pi r^3 / \text{Base area} \times C}$$

$$\text{Base area} = 6 \times \frac{\sqrt{3}}{4} (4r^2)$$

$$C = 4r\sqrt{(2/3)}$$

$$\text{Packing fraction} = \frac{\pi}{3}\sqrt{2} = 0.74$$

$$\text{Void \%} = (1 - 0.74) \times 100 = 26\%$$

185. As 'A' atoms are at eight corners of the cube.

$$\text{So number of A atoms in the unit} = 8 \times 1/8 = 1$$

As 'B' atoms are at the face center of six faces.

So number of B atoms share the unit cell

$$= 6 \times \frac{1}{2} = 3$$

Thus the composition of the substance is  $\text{AB}_3$ .

$$188. \rho = \frac{ZA}{NV}$$

$$Z = \frac{\rho NV}{A} = \frac{2 \times 6 \times 10^{23} \times (5 \times 10^{-8})^3}{75}$$

$$n = 2$$

$$r = \frac{\sqrt{3}}{4} a = \frac{\sqrt{3}}{4} \times 5 = 2.165 \text{ \AA} = 216.5 \text{ pm}$$

the answer may be 216 pm or 217 pm.

## Numericals For Practice

- Aluminium forms face centered cubic crystals. The density of Al is  $2.7 \text{ gm/cm}^3$ . Calculate the length of the side unit cell of Al [At. weight Al = 27]
 

a. 205 Å      b. 405 Å  
c. 805 Å      d. 605 Å
- Calculate the  $\lambda$  of X-rays which give a diffraction angle  $2\theta = 16.80^\circ$  for a crystal. (Given interplanar distance = 0.200 nm; diffraction = first order;  $\sin 8.40^\circ = 0.1461$ )
 

a. 58.4 pm      b. 5.84 pm  
c. 584 pm      d. 648 pm
- An element crystallizes in a body-centered cubic lattice. The edge of the unit cell is 2.86 Å, and the density of the crystal is  $7.92 \text{ g/cm}^3$ . Calculate the atomic weight of the element.
 

a. 50.8      b. 55.8  
c. 55.6      d. 54.8
- The experimental density of cesium chloride is  $3.907 \text{ g/cm}^3$ , and the calculated density  $3.920 \text{ g/cm}^3$ . What is the per cent of empty lattice spaces in a crystal of cesium chloride?
 

a. 0.33 %      b. 0.36 %  
c. 0.30 %      d. 0.38%
- In a crystallizes solid MX, the first order reflections from (100), (110) and (111) faces using monochromatic X- rays are 8.4 and 5.2 respectively. How does the spacing of the three planes vary in the solid MX?
 

a. 1 : 0.705 : 1.14  
b. 1.14 : 0.705 : 1  
c. 0.705 : 1 : 1.14  
d. 2 : 1.14 : 0.705
- RbI crystallizes in b.c.c structure in which each Rb<sup>+</sup> is surrounded by eight iodide ions each of radius 2.17 Å. Find the length of one side of RbI unit cell.
 

a. 2.01 Å      b. 5.01 Å  
c. 4.01 Å      d. 10.5 Å
- The edge length of a face centered cubic lattice of NaCl is 564 pm. What is the density of NaCl in  $\text{g/cm}^3$ ?
 

a. 1.26      b. 0.26  
c. 4.46      d. 2.16
- A metallic element exists as a cubic structure. The edge length of the unit cell is 2.9 Å. The density of the metal is 7.2 g/cc. The number of unit cells in 100 g of the metal would be
 

a.  $5.7 \times 10^{23}$       b.  $11.4 \times 10^{23}$   
c.  $2.85 \times 10^{23}$       d.  $5.7 \times 10^{22}$
- The edge of the unit cell of KCl is  $6.29 \times 10^{-10} \text{ m}$ , and the density of KCl is  $1.99 \times 10^{-3} \text{ kg m}^{-3}$ . If the KCl unit cell is face centered cubic and contains 4 K<sup>+</sup> ions and 4Cl<sup>-</sup>ions per unit cell , then calculate the number of K<sup>+</sup>ions in one kg of KCl.
 

a.  $8.07 \times 10^{25}$       b.  $8.07 \times 10^{-25}$   
c.  $8.07 \times 10^{27}$       d.  $8.07 \times 10^{-27}$
- Gold crystallizes as a face-centered cubic structure. The side of a unit cell is 4.07 Å. What is the radius of a gold atom, assuming the atoms to be in contact in the crystal?
 

a. 1.54 Å      b. 1.48 Å  
c. 1.40 Å      d. 1.44 Å

## 8.46 ■ Solid State

11. Chromium metal crystallizes in a body centred cubic lattice. The length of the unit cell is found to be 287 pm. Calculate atomic radius.
- a. 62.27 pm      b. 124.27 pm  
c. 12.427 pm      d. 120.27 pm
12. At room temperature, polonium crystallizes in primitive cubic unit cell. If  $a = 3.35 \text{ \AA}$ , Find the theoretical density of polonium. Molar mass M of polonium =  $209 \text{ gmo}^{-1}$
- a.  $9.23 \text{ g/cm}^3$       b.  $3.66 \text{ g/cm}^3$   
c.  $9.32 \text{ g/cm}^3$       d.  $9.25 \text{ g/cm}^3$
13. The density of  $\text{CaF}_2$  (fluorite structure) is  $3.18 \text{ g/cm}^3$ . The length of the side of the unit cell is:
- a. 353 pm      b. 444 pm  
c. 546 pm      d. 273 pm
14. In a simple cubic lattice of anions, the side length of the unit cell is  $2.88 \text{ \AA}$ . The diameter of the void in the bond centre is
- a.  $0.661 \text{ \AA}$       b.  $2.108 \text{ \AA}$   
c.  $4.208 \text{ \AA}$       d.  $1.104 \text{ \AA}$
15. Calculate the efficiency of packing in the diamond structure. The unit cell dimension of diamond is  $3.567 \text{ \AA}$ .
- a. 0.3411      b. 0.3409  
c. 0.3407      d. 0.3401
16. Iron crystallizes in a body-centered cubic cell having an edge length of 287 pm. what is the density of iron in  $\text{g/cm}^3$ .
- a. 5.85      b. 3.87  
c. 17.8      d. 7.85
17. A compound with formula  $\text{XY}_2\text{O}_4$  adopts a crystal structure in which  $\text{O}^{2-}$  ions forms ccp arrangement.  $\text{X}^{2+}$  ions occupy octahedral void which  $\text{Y}^{3+}$  ions are distributed equally between tetrahedral and octahedral voids. The fraction of octahedral and tetrahedral voids occupied are respectively
- a. 12.5 %, 50%      b. 50%, 12.5 %  
c. 25%, 75 %      d. 75%, 25%
18. CdO has NaCl structures with density  $8.27 \text{ g/cc}$ . If the ionic radius of  $\text{O}^{2-}$  is  $1.24 \text{ \AA}$ , determine ionic radius of  $\text{Cd}^{2+}$ .
- a.  $1.5 \text{ \AA}$       b.  $1.1 \text{ \AA}$   
c.  $1.8 \text{ \AA}$       d.  $1.3 \text{ \AA}$
19. What is the density of  $\text{KF(s)}$  if it has a NaCl structure and a unit cell length of  $5.35 \times 10^{-10} \text{ m}$ ?
- a.  $1.37 \text{ g/cm}^3$       b.  $2.37 \text{ g/cm}^3$   
c.  $2.47 \text{ g/cm}^3$       d.  $2.57 \text{ g/cm}^3$
20. Volume occupied by one molecule of water (density =  $1 \text{ g cm}^{-3}$ ) is
- a.  $3.0 \times 10^{-23} \text{ cm}^3$   
b.  $5.5 \times 10^{-23} \text{ cm}^3$   
c.  $9.0 \times 10^{-23} \text{ cm}^3$   
d.  $6.023 \times 10^{-23} \text{ cm}^3$
21. The second order Bragg diffraction of X-rays with  $\lambda = 1 \text{ \AA}$  from a set of parallel planes in a metal occurs at an angle of  $60^\circ$ . The distance between the scattering planes in the crystal is
- a.  $2.00 \text{ \AA}$       b.  $1.00 \text{ \AA}$   
c.  $0.575 \text{ \AA}$       d.  $1.15 \text{ \AA}$
22. The atomic radius of lead is  $1.750 \text{ \AA}$ . Lead crystallizes in a face- centered cubic lattice. What is the density of lead?
- a.  $22.35 \text{ g/cm}^3$       b.  $11.33 \text{ g/cm}^3$   
c.  $11.35 \text{ g/cm}^3$       d.  $11.53 \text{ g/cm}^3$
23. Silver crystallizes in a face-centered cubic structure. What is the edge length of the unit cell if the atomic radius of silver is 144 pm?
- a. 203.5 pm      b. 407 pm  
c. 307 pm      d. 147 pm
24. Clausthalite is a mineral composed of lead selenide,  $\text{PbSe}$ , The mineral adopts a  $\text{NaCl}$  – type structure. The density of  $\text{PbSe}$  at  $25^\circ\text{C}$  is  $8.27 \text{ g/cm}^3$ . Find the length of an edge of the  $\text{PbSe}$  unit cell .(molecular weight = 286.2 g)
- a.  $6.44 \text{ \AA}$       b.  $6.13 \text{ \AA}$   
c.  $7.11 \text{ \AA}$       d.  $3.065 \text{ \AA}$
25. Calculate the theoretical density of rhombic sulphur if  $a = 10.4646 \text{ \AA}$ ,  $b = 12.8660 \text{ \AA}$  and  $c = 24.4860 \text{ \AA}$ ,  $Z = 128$  for this unit cell.
- a.  $2.067 \times 10^3 \text{ kg m}^{-3}$   
b.  $2.067 \times 10^3 \text{ kg m}^{-3}$   
c.  $2.067 \times 10^3 \text{ kg m}^3$   
d.  $2.067 \times 10^3 \text{ kg m}^5$
26. Sodium metal adopts bcc structure, the distance between nearest sodium atoms is 367 nm. The edge length of the unit cell is nearly
- a.  $3.67 \text{ \AA}$       b.  $4.18 \text{ \AA}$   
c.  $5.21 \text{ \AA}$       d.  $4.24 \text{ \AA}$
27. At room temperature iron crystallizes in a body-centered cubic close-packed structure. The length of an edge of the cubic cell is 287 pm. A body-centered cubic structure has 2 atoms per unit cell.

Given that the density of Fe is 7.86 g/cm<sup>3</sup>, calculate the mass of an iron atom.

a.  $9.25 \times 10^{-23}$  g /atom

b.  $9.25 \times 10^{23}$  g /atom

c.  $9.25 \times 10^{-24}$  g /atom

d.  $9.25 \times 10^{24}$  g /atom

28. Iron (II) oxide, FeO, crystal and each edge of the unit cell is 5.0 Å. Taking density of the oxide as 4.0 g cm<sup>-3</sup>, calculate the number of Fe<sup>2+</sup> and O<sup>2-</sup> ions present in each unit cell.

- a. 6  
b. 4  
c. 8  
d. 12

29. How many unit cells are present in a cube shaped ideal crystal of NaCl of mass 1.00 g? [Atomic mass of Na = 23, Cl = 35.5]

- a.  $2.57 \times 10^{21}$   
b.  $6.14 \times 10^{21}$   
c.  $3.28 \times 10^{21}$   
d.  $1.71 \times 10^{21}$

30. An unknown metal crystallizes in a body-centered cubic lattice with a unit cell edge length of 3.301 Å. Its density is 8.569 g/cm<sup>3</sup> at 20°C. Identify the metal.

- a. Mo  
b. Y  
c. Fe  
d. Nb

ANSWER KEYS	Q.	Ans.								
	1.	b	2.	a	3.	b	4.	a	5.	a
	6.	b	7.	d	8.	a	9.	c	10.	d
	11.	b	12.	a	13.	c	14.	b	15.	d
	16.	d	17.	b	18.	b	19.	c	20.	a
	21.	d	22.	c	23.	b	24.	b	25.	b
	26.	d	27.	a	28.	b	29.	a	30.	d

## Hints and Explanations

1. Density =  $\rho = \frac{n \times M_m}{M_A \times V}$

here n = no. of atoms in one unit cell

M<sub>m</sub> = molar mass of atom or molecule

For FCC unit cell, n = 4 Atomic weight of Al = 27

$$V = a^3 = \frac{4 \times 27}{6.03 \times 10^{23} \times 2.7}$$

$$a = 4.050 \times 10^{-8} \text{ cm} = 405 \text{ Å}$$

2.  $n \lambda = 2d \sin \theta$

$$(1) (\lambda) = 2 \times 0.2 \times \sin (8.4)$$

$$\lambda = 2 \times 0.2 \times 0.1461$$

$$= 0.05844 \text{ nm}$$

$$= 0.05844 \times 10^{-9} \text{ m}$$

$$= 58.44 \text{ pm} \quad (1 \text{ pm} = 10^{-12} \text{ m})$$

4. Per cent empty lattice spaces

$$= \frac{3.920 - 3.907}{3.907} \times 100$$

$$= 0.33 \%$$

5. According to Bragg's law, we have

$$2d \sin \theta = n\lambda$$

For a first order reflection, n = 1

$$d_{100} = \frac{\lambda}{2 \sin 5.9^\circ}$$

$$= \frac{1}{0.103}$$

## 8.48 ■ Solid State

$$d_{110} = \frac{\lambda}{2 \sin 8.4^\circ}$$

$$= \frac{1}{0.146}$$

$$d_{111} = \frac{\lambda}{2 \sin 5.2^\circ}$$

$$= \frac{1}{0.0906}$$

$$d_{100} : d_{110} : d_{111} = \frac{1}{0.103} : \frac{1}{0.146} : \frac{1}{0.0906}$$

$$= 1 : 0.705 : 1.14$$

6.  $2r_{\text{Rb}}^+ + r_i^- = \sqrt{3} \times a$ ,

where  $a$  = edge length of the cube

From question,

$$r_{\text{Rb}}^+ = 2.17 \text{ \AA} \quad r_i^- = 2.17 \text{ \AA}$$

$$\frac{4 \times 2.17}{\sqrt{3}} \text{ \AA}$$

or,

$$a = 5.01 \text{ \AA}$$

8. Mass of a unit cell =  $V \times d$

$$= (2.9 \times 10^{-8})^3 \times 7.2$$

$$= 1.756 \times 10^{-22} \text{ g}$$

$$\text{Number of unit cells} = \frac{100}{1.756 \times 10^{-22}}$$

$$= 5.7 \times 10^{23}$$

9. Since the edge of unit cell =  $6.29 \times 10^{-10} \text{ m}$

$$\text{The volume of the unit cell} = (6.29 \times 10^{-10})^3 \text{ m}^3$$

$$\text{Further the density of KCl} = 1.99 \times 10^3 \text{ kg m}^{-3}$$

$$\text{Weight of the one unit cell}$$

$$= 1.99 \times 10^3 (6.29 \times 10^{-10})^3 \text{ kg}$$

$$1 \text{ kg of KCl contains}$$

$$= \frac{1}{(6.29 \times 10^{-10})^3 \times 1.99 \times 10^3}$$

Since each unit cell contains  $4K^+$  ions, therefore, the number of  $K^+$  ions present per kg of KCl

$$= 4 \times \frac{1}{(6.29 \times 10^{-10})^3 \times 1.99 \times 10^3}$$

$$= 8.07 \times 10^{27}$$

10. Each face of a unit cell consists of five atoms of gold in contact. The diagonal of the square formed by connecting the centers of the four corner atoms is  $4r$ , where  $r$  is the radius of a gold atom. also, the diagonal of the square formed would be  $(4.07 \times \sqrt{2}) \text{ \AA}$ . Equating the two values we have:

$$4r = (4.07 \times \sqrt{2}) \text{ \AA}$$

$$= 1.44 \text{ \AA} = \text{radius of gold atom.}$$

11. For b.c.c structure

$$4r = \sqrt{3} \times a$$

$$\Rightarrow 4r = \sqrt{3} \times 287 \text{ pm}$$

$$\Rightarrow r = \frac{\sqrt{3} \times 287}{4} \text{ pm}$$

$$\Rightarrow r = 124.27 \text{ pm}$$

12. Volume,  $V = a^3 = (3.35 \text{ \AA})^3 = (3.35 \times 10^{-8} \text{ cm})^3$

$$\rho = \frac{nM}{N_A V}$$

$$= \frac{(1) (209 \text{ g mol}^{-1})}{(6.022 \times 10^{23} \text{ mol}^{-1}) (3.35 \times 10^{-8} \text{ cm})^3}$$

$$= 9.23 \text{ g/cm}^3$$

13.  $\rho = \frac{Z.M}{N_A \cdot a^3}$

$$Z = 4; M = 40 + 2 \times 19$$

14. Body diagonal of cubic lattice =  $a\sqrt{3}$

$$\text{Diameter of the void in the body center}$$

$$= a\sqrt{3} - a$$

$$= (1.732 \times 2.88) - 2.88$$

$$= 4.988 - 2.88 = 2.108 \text{ \AA}$$

17. Here number of  $O^{2-}$  ions per unit cell

$$= \frac{8}{8} + \frac{6}{2} = 4$$

Tetrahedral voids = 8;

Octahedral voids = 4;

Octahedral voids occupied by  $X^{2+}$  = 1

Octahedral voids occupied by  $Y^{3+}$  = 1,

Total octahedral voids occupied = 2

Total tetrahedral voids occupied = 1

18.  $8.27 = \frac{4 \times 128}{6.023 \times 10^{23} a^3}$

$$a = 46.8 \times 10^{-9} \text{ cm}$$

$$= 4.68 \text{ \AA}$$

$$= 2[r_{\text{O}_2}^{2-} + r_{\text{Cd}}^{2+}]$$

$$r_{\text{Cd}}^{2+} = 1.1 \text{ \AA}$$

20. Weight of  $6.023 \times 10^{23}$  molecule of water = 18 g

As volume occupied by  $6.023 \times 10^{23}$  molecule of water (density = 1 g cm<sup>-3</sup>) will be

$$= \frac{18 \text{ g}}{1 \text{ g cm}^{-3}} = 18 \text{ cm}^3 \text{ or ml}$$

So volume occupied by one molecule of water

$$= \frac{18}{6.023 \times 10^{23}} = 2.988 \times 10^{-23}$$

$$= 3.0 \times 10^{-23} \text{ cm}^3$$

21.  $n\lambda = 2d \sin \theta$

$$2 \times 1 = 2 \times d \sin \theta$$

$$2 = 2d \frac{\sqrt{3}}{2} \quad (\sin 60^\circ = \sqrt{3}/2)$$

$$d = 2/\sqrt{3} = 1.15 \text{ \AA}$$

24.  $d = \frac{Z \times M}{(a)^3 \times N_A}$

$$(a) \frac{3}{d} = \frac{Z \times M}{d \times N_A}$$

$$= \frac{4 \times 286.2}{8.27 \times 6.02 \times 10^{23}}$$

on solving

$$a^3 = 229.8 \text{ \AA}$$

$$a = (229.87)^{1/3} \text{ \AA}$$

$$= 6.13 \text{ \AA}$$

26. For bcc structure of atoms, the nearest atoms touch along body diagonal.

Distance between nearest atoms

$$= 2r = \frac{2 \times \sqrt{3} a}{4}$$

$$a = \frac{2 \times d}{\sqrt{3}}$$

$$= \frac{2 \times 3.67}{\sqrt{3}}$$

$$= 4.24 \text{ \AA}$$

27. The length of an edge of the cubic unit cell of iron is 287 pm, or  $287 \times 10^{-12} \text{ m} = 2.87 \times 10^{-8} \text{ cm}$ . From this length, the volume of the cubic cell of iron is calculated:

$$V = 1 \times 1 \times 1 = l^3 = (2.87 \times 10^{-8} \text{ cm})^3$$

$$= 2.36 \times 10^{-23}$$

$$\text{Now mass} = d \times V$$

$$= 7.86 \times 2.36 \times 10^{-23}$$

$$= 1.85 \times 10^{-22}$$

$$\text{As no. of atoms per unit cell} = 2$$

$$\text{So mass of 1 atom} = \frac{1.85 \times 10^{-22}}{2}$$

$$= 9.25 \times 10^{-23} \text{ g /atom}$$

28. Volume of the unit cell =  $(5 \times 10^{-8} \text{ cm})^3$

$$= 1.25 \times 10^{-22} \text{ cm}^3$$

$$\text{Density of FeO} = 4.0 \text{ g/cm}^3$$

$$\text{Mass of the unit cell} = 1.25 \times 10^{-22} \text{ cm}^3 \times 4.0 \text{ g/cm}^3$$

$$= 5.0 \times 10^{-22} \text{ g}$$

$$\text{Mass of one molecule of FeO}$$

$$= \text{Molar mass in grams}$$

$$\text{Avogadro's number}$$

$$= \frac{72 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$= 1.195 \times 10^{-22} \text{ g}$$

$$\text{Number of FeO molecules per unit cell}$$

$$= \frac{5.0 \times 10^{-22} \text{ g}}{1.195 \times 10^{-22} \text{ g}}$$

$$= 4.19 \approx 4$$

29. Mass of one unit cell (m)

$$= \text{volume} \times \text{density}$$

$$= a^3 \times d$$

$$= \frac{a^3 \times Mz}{N_0 a^3} = \frac{Mz}{N_0}$$

$$m = \frac{58.5 \times 4}{6.02 \times 10^{23}} \text{ g}$$

$$\text{Number of unit cells in 1 g} = 1 \text{-----}/\text{m}$$

$$= \frac{6.02 \times 10^{23}}{58.5 \times 4} = 2.57 \times 10^{21}$$

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## CHAPTER 9

# Solutions and Colligative Properties

### Chapter Contents

Raoult's law; Molecular weight determination from lowering of vapour pressure, elevation of boiling point and depression of freezing point and Various levels of multiple-choice questions.

### SOLUTION

Solution is a homogeneous mixture of two or more chemically non-reacting substances whose composition can be varied within certain limits.

A solution which contains only two components is called a *binary solution*.

The component which is present in smaller amount is called the solute and the other present in larger amount is called the *solvent*.

### Vapour Pressure of a Liquid

It is the pressure exerted by vapours when in equilibrium with the liquid at a given temperature. It depends upon nature of liquid and temperature. Pure liquid has always a vapour pressure greater than its solution.

Vapour pressure of a liquid helps us to have an ideal of forces of attraction amongst the molecules of liquid that is, more the force of attraction, lower is the vapour pressure and vice versa.

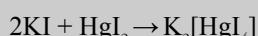
- Vapour pressure of a liquid increases with a increase in temperature due to increase in kinetic energy of solvent molecules that is, increase in evaporation however it is independent of the nature of the vessel.

The variation of vapour pressure with temperature can be given by Clausius-Clapeyron equation as follows:

$$\log_{10} \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303 R} \cdot \frac{T_2 - T_1}{T_1 T_2}$$

### REMEMBER

Addition of  $HgI_2$  to  $KI_{(aq)}$  shows an increase in vapour pressure due to complex formation number of spears present in solution decreases.



## Vapour Pressure of a Solution

When a miscible solute is added to a pure solvent, it results in the formation of solution. As some molecules of solute will replace the molecules of the solvent from the surface, therefore, escaping tendency of solvent molecules decreases. This causes a lowering of vapour pressure.

- The vapour pressure of a solution is less than that of pure solvent.
- If vapour pressure of solvent is  $P$  and that of solution is  $P_s$  then lowering of V.P. =  $P - P_s$ .
- Vapour pressure of solution decreases as surface area occupied by solvent molecule decreases and density increases.

## RAOULT'S LAW

### Raoult's Law for Volatile Solutes

Raoult's law states that in a solution, the vapour pressure of a component at a given temperature is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of that component in the pure state.

The total vapour pressure  $P$  of a solution containing two components A and B is

$$P_A = P_A^o \times X_A$$

$$P_B = P_B^o \times X_B$$

Suppose a solution is obtained by mixing two volatile components A and B. If their vapour pressure in pure states are  $P_A$ ,  $P_B$  respectively and mole fraction are  $X_A$  and  $X_B$  respectively then their partial pressures  $P_A$ ,  $P_B$  can be given or

$$P = P_A + P_B = P_A^o X_A + P_B^o X_B$$

$$\text{As } X_A = \frac{n_A}{n_A + n_B}$$

$$X_B = \frac{n_B}{n_A + n_B}$$

$$\boxed{\text{So } P_{\text{Sol.}} = \frac{n_A}{n_A + n_B} \cdot P_A^o + n_B \frac{P_B^o}{n_A + n_B}}$$

Here  $n_A$  and  $n_B$  represents moles of A and B respectively.

As we know that

$$X_A + X_B = 1$$

$$X_A = (1 - X_B)$$

$$P = (1 - X_B) P_A^o + P_B^o X_B$$

$$P = (P_B^o - P_A^o) X_B + P_A^o$$

## Composition of the Vapour

The composition of the liquid and vapour that are in mutual equilibrium are not necessarily the same. The mole fraction in vapour phase is high for more volatile component.

Suppose the mole fraction of A and B in vapour phase be  $Y_A$  or  $N_A$  and  $Y_B$  or  $N_B$ .

According to Dalton's law,

$$Y_A \text{ or } N_A = \frac{P_A}{P_T} = \frac{P_A^o X_A}{P_A^o X_A + P_B^o X_B}$$

$$Y_B \text{ or } N_B = \frac{P_B}{P_T} = \frac{P_B^o X_B}{P_A^o X_A + P_B^o X_B}$$

### REMEMBER

- (i) From here, we can say that the total V.P of the solution can be related to the mole fraction of any component.
- (ii) Total vapour pressure over the solution varies linearly with the mole fraction of component also.
- (iii) **Raoult's Law as a special case of Henry's Law** As according to Raoult's law, the vapour pressure of a volatile component in a given by Henry's law which is given as  $P = K_H X$ .

On comparing both these equations for Raoult's law and Henry's law, it can be said that the partial pressure of the volatile component or gas is directly proportional to its mole fraction in solution. Only the proportionality constant  $K_H$  differs from  $P_A^o$ . Thus, Raoult's law becomes a special case of Henry's law in which  $K_H$  becomes equal to  $P_A^o$

## Illustrations

1. Two liquids A and B on mixing form an ideal solution. At 30°C, the vapour-pressure of the solution containing 3 mol of A and 1 mol of B is 550 mm Hg. But when 4 mol of A and 1 mol of B are mixed, the vapour pressure of the solution thus formed is 560 mm Hg. What would be the vapour pressure of pure A and B at this temperature?

**Solution**  $P_A = P_{A}^o \cdot x_A = P_{A}^o \times \frac{n_A}{n_A + n_B}$

$$P_B = P_B^o \cdot x_B = P_B^o \times \frac{n_B}{n_A + n_B}$$

- (i) For a solution having 3 mol of A and 1 mol of Y

$$P_{\text{total}} = P_A + P_B$$

$$= P_A^o \times \frac{(3 \text{ mol})}{3 + 1 \text{ mol}} + P_B^o \times \frac{(1 \text{ mol})}{3 + 1 \text{ mol}}$$

$$550 = \frac{3}{4} P_A^o + \frac{1}{4} P_B^o$$

$$2200 = 3 P_A^o + P_B^o \dots\dots\dots (i)$$

- (ii) For a solution having 4 mol of A and 1 mol B.

$$P_{\text{total}} = P_A + P_Y$$

$$= P_A^o \times \frac{4 \text{ mol}}{4 + 1 \text{ mol}} + P_B^o \times \frac{1 \text{ mol}}{4 + 1 \text{ mol}}$$

$$560 = \frac{4}{5} P_A^o + \frac{1}{5} P_B^o$$

$$2800 = 4 P_A^o + P_B^o \dots\dots\dots (ii)$$

On subtracting equation (i) from (ii), we get

$$P_A^o = 600 \text{ mm Hg}$$

On substituting the value of  $P_A^o = 600 \text{ mm Hg}$

$$2200 = 3 \times 600 + P_B^o$$

$$P_B^o = 2200 - 1800 = 400 \text{ mm Hg.}$$

2. Benzene ( $C_6H_6$ ) and toluene ( $C_7H_8$ ) form a nearly ideal solution. At a certain temperature the vapour pressure of pure benzene is 150 mm Hg and of pure toluene is 50 mm Hg. For this temperature, calculate the vapour pressure of the solution containing equal weights of the two substances.

**Solution** Suppose the mass of benzene = W g

$$\text{Mass of toluene} = W \text{ g}$$

$$\text{Molecular mass of benzene} = 78 \text{ g/mol}$$

$$\text{Molecular mass of toluene} = 92 \text{ g/mol}$$

$$\text{Moles of benzene} = W/78 \text{ mol}$$

$$\text{Moles of toluene} = W/92 \text{ mol}$$

$$\text{Total moles} = \frac{W}{78} + \frac{W}{92}$$

$$= \frac{92W + 78W}{78 \times 92} = \frac{170W}{78 \times 92}$$

$$\text{Mole fraction of benzene} = \frac{\frac{W}{78}}{\frac{170W}{78 \times 92}}$$

$$x_A = \frac{W}{78} \times \frac{78 \times 92}{170W} = \frac{92}{170} = 0.541$$

$$\text{Mole fraction of toluene} = 1 - 0.541 \\ = 0.459$$

Partial vapour pressure of benzene

$$= (P_{\text{benzene}}^o \cdot x_{\text{benzene}})$$

$$= 150 \times 0.541 = 81.150 \text{ mm}$$

Partial vapour pressure of toluene

$$= (P_{\text{toluene}}^o \cdot x_{\text{toluene}})$$

$$= 50 \times 0.459 = 22.950 \text{ mm}$$

Total vapour pressure of solution

$$= 81.18 + 22.95 = 104.10 \text{ mm}$$

3. The vapour pressures of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature

## 9.4 ■ Solutions and Colligative Properties

by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour.

**Solution** Mol. mass of  $\text{C}_2\text{H}_5\text{OH}$  = 46

$$\text{Number of moles of } \text{C}_2\text{H}_5\text{OH} = \frac{60}{46} = 1.304$$

$$\text{Mol. mass of } \text{CH}_3\text{OH} = 32$$

$$\text{Number of moles of } \text{CH}_3\text{OH} = \frac{40}{32} = 1.25$$

$$X_A \text{ mole fraction of } \text{C}_2\text{H}_5\text{OH} = \frac{1.304}{1.304 + 1.25} \\ = 0.5107$$

$$X_B \text{ mole fraction of } \text{CH}_3\text{OH} = \frac{1.25}{1.304 + 1.25} \\ = 0.4893$$

$$\text{Partial pressure of } \text{C}_2\text{H}_5\text{OH.} = X_A \cdot P_A^o \\ = 0.5107 \times 44.5$$

$$= 22.73 \text{ mm Hg}$$

$$\text{Partial pressure of } \text{CH}_3\text{OH} = X_B \cdot P_B^o$$

$$= 0.4893 \times 88.7$$

$$= 43.40 \text{ mm Hg}$$

Total vapour pressure of solution

$$= 22.73 + 43.40$$

$$= 66.13 \text{ mm Hg}$$

Mole fraction of  $\text{CH}_3\text{OH}$  in the vapour

$$= \frac{\text{Partial pressure of } \text{CH}_3\text{OH}}{\text{Total vapour pressure}}$$

$$= \frac{43.40}{66.13} = 0.6563$$

### (b) Raoult's Law for Non-Volatile Solutes

Raoult's law states that the relative lowering of vapour pressure of solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution.

$$\frac{P^o - P_S}{P^o} = \frac{n_2}{n_1 + n_2} = X_2$$

Here  $X_2$  = mole fraction of solute

$n_1$  = moles of solvent,  $n_2$  = moles of solute

$P_S$  = vapour pressure of the solution

$P^o$  = vapour pressure of pure solvent

**Note:** Explanation is given further

### Illustrations

4. (a) 10 g of a certain non-volatile solute were dissolved in 100 g water at 20°C. The vapour pressure was lowered from 17.3555 mm to 17.2350 mm, calculate molecular weight of solute.

(b) The vapour pressure of pure water at 25°C is 23.62 mm. What will be the vapour pressure of a solution of 1.5 g of urea in 50 g of water?

**Solution** (a) 
$$\frac{P^o - P_S}{P^o} = \frac{n}{N} = \frac{w}{m} \times \frac{M}{W}$$

$$\text{Given: } P^o = 17.3555 \text{ mm}$$

$$P_S = 17.2350 \text{ mm}$$

$$w = 10 \text{ g}$$

$$W = 100 \text{ g}$$

$$M = 18 \text{ g}$$

$$\frac{17.3555 - 17.2350}{17.3555} = \frac{10 \times 18}{m \times 100}$$

$$m = 257.45$$

$$(b) \frac{P^o - P_S}{P^o} = \frac{w}{m} \times \frac{M}{W}$$

$$\frac{23.62 - P_S}{23.62} = \frac{1.5 \times 18}{60 \times 50}$$

$$P_S = 23.41 \text{ mm.}$$

5. A solution containing 30 g of a non-volatile solute in exactly 90 g water has a vapour pressure of 21.85 mm of Hg at 25°C. Further 18 g of water is then added to solution, the new vapour pressure becomes 22.15 mm of Hg at 25°C. Calculate,

- (a) Molecular weight of solute
- (b) Vapour pressure of water at 25°C.

**Solution**  $\frac{P^o - 21.85}{21.85} = \frac{30 \times 18}{90 \times m} \dots\dots (i)$

$$\text{Weight of solvent} = 90 + 188 = 108 \text{ g}$$

$$\frac{P^o - 22.15}{22.15} = \frac{30 \times 10}{108 \times m} \dots\dots (ii)$$

From equation (i)

$$P^o_M - 21.85 m = 21.85 \times 6 = 131.1$$

From equation (ii)

$$P^o_M - 22.15 m = 22.15 \times 5 = 110.75$$

On subtracting equation (ii) from equation (i), we get

$$0.30 m = 20.35$$

$$m = \frac{20.35}{0.30} = 67.83$$

On substituting the value of m in equation (i)

$$\frac{P^o - 21.85}{21.85} = 3 \frac{0 \times 18}{90 \times 67.83}.$$

$$P^o = 23.78 \text{ mm.}$$

## IDEAL SOLUTIONS

Ideal solutions are the solutions in which solute-solute and solvent-solvent interactions are almost similar to solute-solvent interactions (A – B = A – A or B – B interactions) and such solutions satisfy the following requirements:

1. They obey Raoult's law for all ranges of concentrations and temperature.

2.  $\Delta H(\text{mix}) = 0$
3.  $\Delta V(\text{mix}) = 0$
4. Here  $(\text{V.P.})_{\text{obs.}} = (\text{V.P.})_{\text{exp.}}$   
 $(\text{B.P.})_{\text{obs.}} = (\text{B.P.})_{\text{exp.}}$

$$P_A = P_A^o X_A,$$

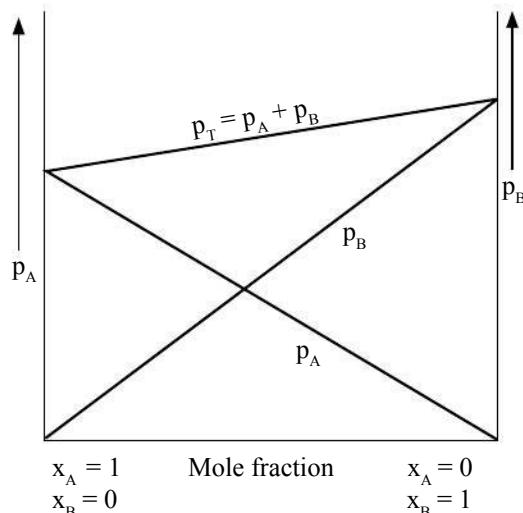
$$P_B = P_B^o X_B,$$

$$P_T = P_A + P_B$$

5. No dissociation or association takes place here.
6. No chemical reaction between solute and solvent.
7. It does not form azeotrope.

### Examples,

1. benzene + toluene
2. hexane + heptane
3. ethyl bromide + ethyl iodide
4. chlorobenzene + bromobenzene etc
5. all dilute solutions
6.  $\text{CCl}_4 + \text{SiCl}_4$
7. Ethylene dichloride + Ethylene di-bromide



Vapour Pressure Diagram for Ideal Solution

## NON-IDEAL SOLUTIONS

Non-ideal solutions are the solutions in which solute-solvent interactions are different from solutesolute and solvent-solvent interactions. These solution do not obey Raoult's law for all concentrations and

1.  $\Delta H \text{ (mix)} \neq 0$
2.  $\Delta V \text{ (mix)} \neq 0$

### Types of non-ideal solutions

- (a) **Non-ideal solutions showing positive deviations:** Positive deviation occurs when total vapour pressure for any mole fraction is more than what is expected according to Raoult's law. This happens when the new interactions are weaker than the interaction in the pure component ( $A - B < A - A$  or  $B - B$  interactions).

- $\Delta H = +ve, \Delta V = +ve$
- It forms minimum boiling azeotrops, for example,  $C_2H_5OH + cyclohexane$ . The H bonding present in pure  $C_2H_5OH$  are cut off on adding cyclohexane. For such solution,  $\Delta V$  and  $\Delta H$  are positive.

Here  $(V.P)_{\text{obs.}} > (V.P)_{\text{exp.}}$

$$(B.P)_{\text{obs.}} < (B.P)_{\text{exp.}}$$

$$P_A > P_A^{\circ} \cdot X_A$$

$$P_B > P_B^{\circ} \cdot X_B$$

$$P_T > P_A^{\circ} X_A + P_B^{\circ} X_B$$

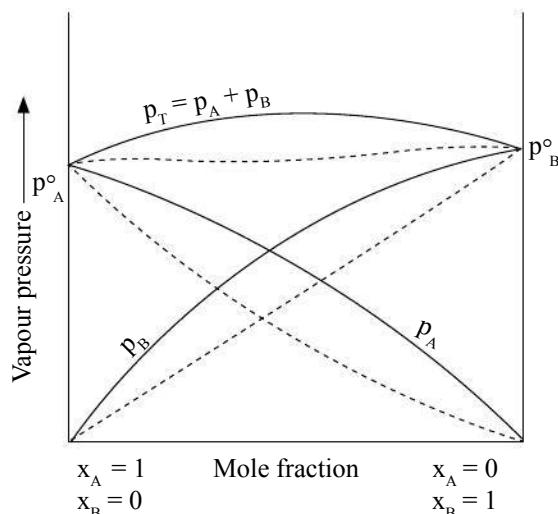
- Here Hydrogen bonds are broken or weakened. Here  $\Delta S$  is more while  $\Delta G$  has less  $-ve$  value and the values of other colligative properties also decrease.
- Here minimum boiling point azeotrop mixture is formed.

#### Example,

1.  $C_2H_5OH + cyclohexane$ .
2. Acetone + carbon disulphide,
3. Acetone + benzene
4. Acetone + Ethylalcohol
5. Carbon tetrachloride + chloroform or Toluene

6. Methylalcohol + water

7. Water + Ethylalcohol



P-x graph for non-ideal solution showing +ve deviation

- (b) **Non-ideal solutions showing negative deviations:** Negative deviation is seen when total vapour pressure for any mole fraction is less than that expected from Raoult's law. This happens when the new interactions are stronger than the interactions in the pure components ( $A - B > A - A$  or  $B - B$  interactions).

- $\Delta H = -ve, \Delta V = -ve$
- It forms maximum boiling azeotrope, for example,  $CHCl_3 + CH_3COCH_3$ . For such solutions  $\Delta V$  and  $\Delta H$  are negative.

#### Example,

1. Chloroform + benzene
2. Acetone + aniline
3. Nitric acid  $(HNO_3)_3 + water$
4. Acetic acid + pyridine

It does not obeys Rault's Law

- H is  $-ve$ , (Heat is evolved here)
- V = is  $-ve$  ( volume decrease as force increases)
- It forms maximum boiling azeotrop.

Here  $(V.P)_{\text{obs.}} < (V.P)_{\text{exp.}}$

$(B.P)_{\text{obs.}} > (B.P)_{\text{exp.}}$

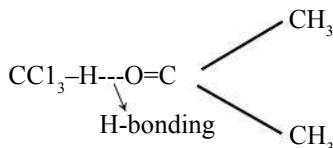
$$P_A < P_A^o \cdot X_A$$

$$P_B < P_B^o \cdot X_B$$

$$P_T < P_A^o X_A + P_B^o X_B$$

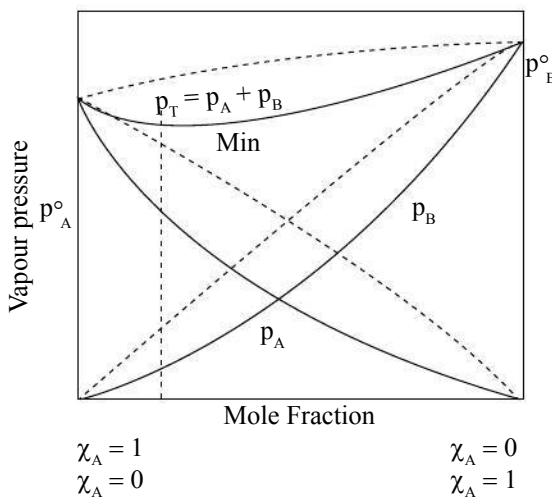
Here  $\Delta S$  has less value while  $\Delta G$  has more -ve value and the values of other colligative properties increase.

Example,  $\text{CHCl}_3 + \text{CH}_3\text{COCH}_3$ .



Here due to Hydrogen bond formation, interaction increases so a negative deviation is observed as escaping tendency of molecules decreases.

1. Chloroform + benzene
2. Acetone + aniline
3. HCl or  $\text{HNO}_3$  + water
4. Acetic acid + pyridine
5. Chloroform + EthylEther
6.  $\text{CH}_3\text{OH}$  + Acetone



## Azeotropic Mixture

An azeotropic mixture is a mixture of two liquids having the same boiling point. These two liquids cannot be separated by simple distillation because of similar boiling point of the liquids. These mixtures are thus called constant boiling mixtures. These are formed by non-ideal solutions.

## Azeotropic Mixture and Composition Curves

These are the mixture of two liquids which boils at one particular temperature like a pure liquid and distils over in the same composition that is, these are constant boiling mixtures. These are formed by non-ideal solutions. The study of the vapour pressure curves of such miscible liquids is of great help in separating the constituents of the liquid mixtures by distillation.

The separation by fractional distillation is possible only when the vapour phase has a composition different from that of the boiling liquid mixture.

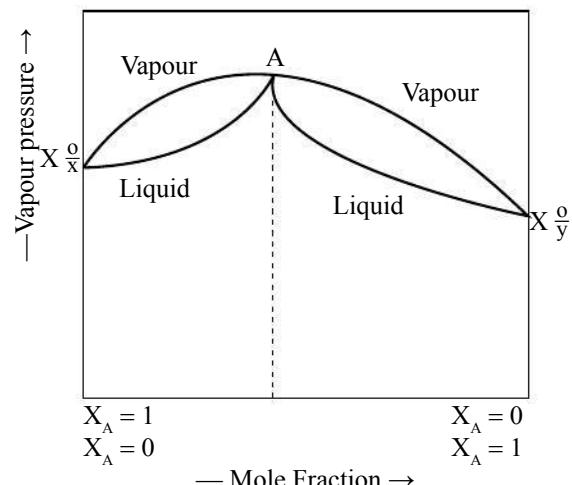
## Types of Azeotropic Mixtures

It is of the following types:

### Azeotropic Mixtures with Minimum Boiling Point

The mixture of two liquids whose boiling point is less than either of the two pure components.

- This is formed by that composition of a non-ideal solution showing positive deviation for which the vapour pressure is maximum.
- Example, Ethanol (95.5%) + water (4.5 %) mixture boils at 351.5 K.
- Such mixtures on distillation will give first fraction upto point M in pure state. After this the temperature will rise and the second component will pass over. Hence in such solutions also complete separation is not possible.



## 9.8 ■ Solutions and Colligative Properties

- The figure shows maximum vapour pressure at point M and therefore solution has lowest boiling point.

### Azeotropic Mixtures with Maximum Boiling Point

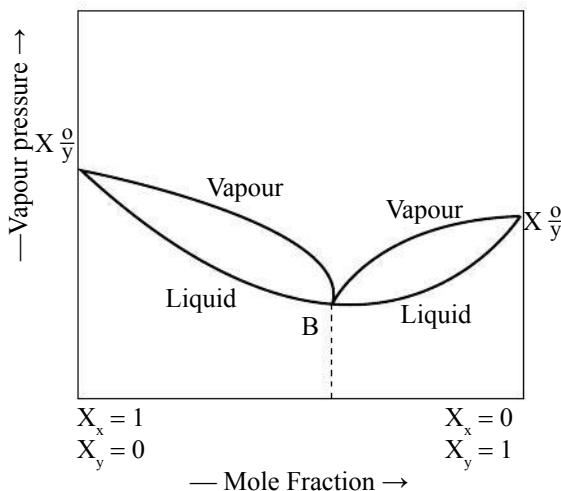
The mixtures of two liquids whose boiling point is more than either of the two pure components.

- This is formed by that composition of a non-ideal solution showing negative deviation for which the vapour pressure is minimum.

Example,  $\text{HNO}_3$  (68%) + water (32%) mixture boils at 393.5 K.

Example, an aqueous solution of hydrochloric acid when subjected to distillation gives initially pure water and later forms a constant boiling mixture at 100°C which contains 20.24 % acid.

- In a mixture of two volatile liquids A and B, if A is more volatile and present in excess, then during distillation the vapours will be rich of component A and the liquid part will be richer in component B. Finally, we reach the point N where vapour pressure is minimum and the boiling point is maximum as shown in the figure.

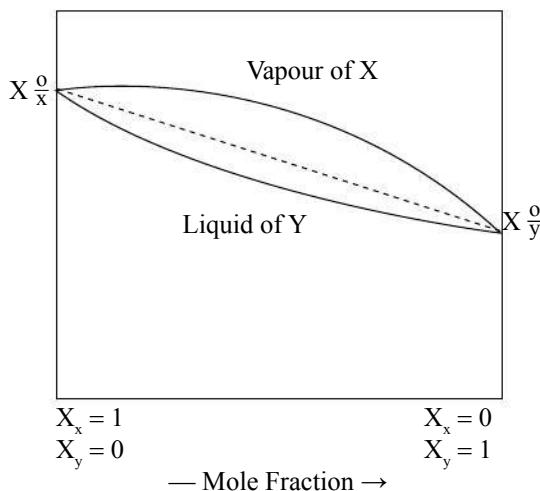


- At this stage, the mixture distills unchanged in composition that is, complete separation of components from this type of solution into pure state is impossible.

### Mixture Showing Ideal Behaviour or Zeotropic Mixture

Those liquid mixtures which distill with a change in composition are called zeotropic mixture. For this type

of mixtures containing liquids A and B, vapour pressure composition curve is a straight line. On distillation, A being more volatile, will collect as distillate.



- The remaining fraction will be poorer in A and richer in B. By repeating the process of distillation again and again, we can get both the components in pure state, example, methanol-water mixture.

### Colligative Properties

Colligative properties are properties of a solution which depend only on the number of particles like ions or molecules of the solute in a definite amount of the solvent but not on the nature of the solute.

Colligative properties are mainly for dilute solutions (Ideal Solutions), non-volatile solute, and process involving no dissociation or association.

Colligative Properties  $\propto$  No. of species

$$\alpha \frac{1}{M} \text{ (Molar mass)}$$

These are as follows:

- Relative lowering of vapour pressure
- Osmotic pressure
- Elevation in boiling point
- Depression in freezing point

\*\* Osmosis, Diffusion, B.P., F.P., V.P. are not Colligative Properties.

### Relative Lowering of Vapour Pressure

When a non-volatile solute is added in a volatile solvent, the vapour pressure of the solution decreases

or becomes less than the vapour pressure of pure solvent. It is due to the increase in density and decrease in naked surface area which decreases rate of evaporation.

$$\text{As rate of evaporation } \propto \frac{1}{\sqrt{d}}$$

If  $P^o$  is vapour pressure of pure solvent and  $P$  is vapour pressure of solvent in solution than the lowering of vapour pressure ( $\Delta p$ ) is given as

$$\Delta P = (P^o - P)$$

The relative lowering of vapour pressure is defined the ratio between lowering of vapour pressure and the vapour pressure of pure solvent.

$$\frac{\Delta P}{P^o} = \frac{P^o - P}{P^o} = \text{Relative lowering of V.P}$$

⇒ When a solution is prepared by mixing the non volatile solute B and solvent A.

$$X_A + X_B = 1$$

$$X_B = 1 - X_A$$

Here  $X_B$  and  $X_A$  are the mole fraction of solute and solvent respectively.

$$\text{As } \frac{P_A}{P_A^o} = X_A$$

$$1 - \frac{P_A}{P_A^o} = 1 - X_A = X_B$$

or

$$\frac{P_A^o - P_A}{P_A^o} = X_B = \frac{\Delta P}{P_A^o} = \frac{n}{n+N}$$

Here  $n$  = number of moles of solute

$N$  = number of moles of solvent

$P_A^o$  = V.P of pure solvent

$P_A$  = V.P of solution

In dilute solution  $N > > n$  and hence

$$X_B = \frac{n}{N} = \frac{w}{m/W/M} = \frac{wM}{Wm}$$

Here  $w$  = weight of solute

$W$  = weight of solvent

$m$  = molecular weight of solute

$M$  = molecular weight of solvent

$$\text{So } \frac{P_A^o - P_A}{P_A^o} = \frac{\Delta P}{P^o} = \frac{wM}{Wm}$$

In place of this relation we can also use this alternative relation

$$\frac{P_A^o - P_A}{P_A} = \frac{W \times M}{W \times M}$$

It is better to use this relation as it gives more accurate value

⇒ If molarity is asked used the relation given below

$$\frac{P_A^o - P_A}{P_A} = \frac{m \times M}{1000}$$

Or

$$m = \left( \frac{P_A^o - P_A}{P_A} \right) \times \frac{1000}{M}$$

- The molecular weight of solute can be determined with the help of the relative lowering of vapour pressure method.

### Measurement of lowering of Vapour Pressure using Ostwald and Walker Method

Here a current of pure air is bubbled through the series of bulbs according to the adjacent figure. The air first get's saturated with the vapours and carries some amount of vapours ( $\alpha$ V.P of solute) and later carries more amount of vapours( $\alpha P_A^o - P_A$ ). Now these sets of bulbs and guard tube having  $\text{CaCl}_2$  are weighted.

Here loss in mass of solution bulbs  $\propto P_A$  or  $P_s$

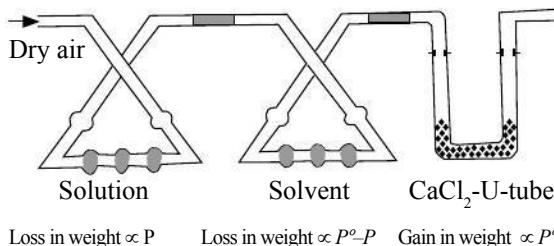
loss in mass of solvent bulbs  $\propto P^o - P_s$  or  $P_A^o - P_A$

Total loss in mass of both sets of bulbs  $\propto P^o$  or  $P_A^o$  or

Gain in mass of  $\text{CaCl}_2$  guard tube

## 9.10 ■ Solutions and Colligative Properties

Hence



$$\text{Loss in weight} \propto P \quad \text{Loss in weight} \propto P^\circ - P \quad \text{Gain in weight} \propto P^\circ$$

$$\frac{P^\circ - P_s}{P^\circ} = \frac{\text{loss in mass of solvent bulb}}{\text{gain in mass of } \text{CaCl}_2 \text{ guard tube}}$$

Or

$$\frac{P^\circ - P_{A_0}}{P}$$

### Illustrations

6. The vapour pressure of pure benzene at  $25^\circ\text{C}$  is 639.7 mm Hg and the vapour pressure of a solution of a solute in benzene at the same temperature is 631.9 mm Hg. Calculate the molality of the solution.

**Solution** Let  $n$  moles of solute are dissolve in 1000 g of benzene

$$\text{Number of moles of solvent (N)} = \frac{1000}{78}$$

$$\frac{p - p_s}{p} = \frac{n}{N}$$

$$\frac{639.7 - 631.9}{639.7} = \frac{n}{1000/78}$$

$$\frac{7.8}{639.7} = \frac{n \times 78}{1000}$$

$$n = \frac{7.8 \times 1000}{639.7 \times 78}$$

$$= 0.156 \text{ m}$$

7. The vapour pressure of pure water at  $30^\circ\text{C}$  is 31.50 mm Hg. When 3.0 g of a non-volatile solute was dissolved in 54 g of water, the vapour pressure of the solution was found to be 31.30 mm Hg. Calculate the molar mass of the solute.

**Solution** Given:  $P_A^\circ = 31.50 \text{ mm}$ ,  $P_A = 31.30 \text{ mm}$ ,

$$W_B = 3.0 \text{ g}, W_A = 54 \text{ g}, M_B = ?$$

$$M_A = 2 \times 1 + 16 = 18 \text{ g/mol}$$

$$\frac{P_A^\circ - P_A}{P_A^\circ} = x_B = \frac{\frac{W_B \cdot M_B}{W_A + W_B}}{M_A \cdot M_B}$$

$$\frac{31.50 - 31.30}{31.50} = \frac{3/M_B}{54 + \frac{3}{M_B}}$$

$$\frac{0.20}{31.50} = \frac{(3/M_B) \times (18 M_B)}{54 M_B + 18 \times 3}$$

$$\frac{54}{54 M_B + 54} = \frac{1}{M_B + 1}$$

$$0.20 (M_B + 1) = 31.50 \times 1$$

$$0.20 M_B + 0.20 = 31.50$$

$$0.20 M_B = 31.50 - 0.20 = 31.30$$

$$M_B = \frac{31.30}{0.20} = 156.5 \text{ g/mol}$$

8. The vapour pressure of an aqueous solution of glucose is 750 mm of Hg at  $373 \text{ K}$ . Calculate the molality and mole fraction of solute.

**Solution** At  $373 \text{ K}$  vapour pressure of water = 760 mm

$$\frac{p - ps}{p} = \frac{w \times M}{m \times W}$$

$$\frac{p - ps}{p} \times \frac{1000}{M} = \text{Molality}$$

$$\frac{760 - 750}{760} \times \frac{1000}{18} = \text{molality of solution}$$

$$\text{Molality of solution} = 0.73 \text{ m}$$

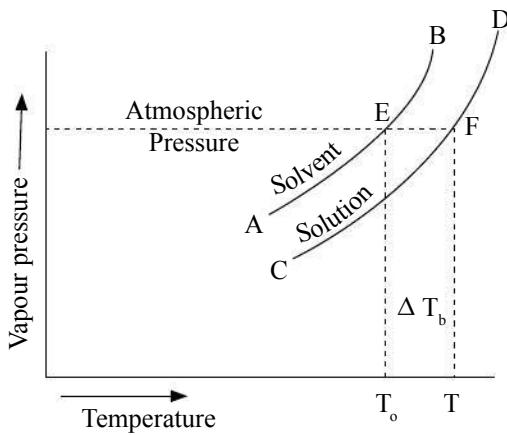
$$\frac{p - ps}{p} = \frac{n}{n + N}$$

$$\text{Mole fraction of solute} = \frac{p - ps}{p}$$

$$= \frac{760 - 750}{760} = \frac{10}{760} = 0.0131$$

## Elevation in Boiling Point

**Boiling Point:** It is the temperature of a liquid at which its vapour pressure becomes equal to the atmospheric pressure. As vapour pressure of solution is lower than that of the solvents. As on addition of a non-volatile solute in a pure solvent it's V.P decreases or V.P of solvent in pure state is more than that of solution. Now in order to boil the solution it is necessary to increase the temperature of solution above the B.P. of pure solvent. It means B.P. of solution is always higher than B.P. of pure solvent. This increase in B.P. of solution is called elevation in B.P. ( $\Delta T_b$ )



**Elevation in boiling point**

- It is also termed as Ebullioscopy.
- It is measured by Lands Berger's method and Koltrell's method.
- Suppose  $T_{b, \text{solvent}}$  and  $T_{b, \text{solution}}$  are the B.P. of pure solvent and solution respectively than elevation in B.P. ( $\Delta T_b$ ) is given as  $\Delta T_b = T_{b, \text{solution}} - T_{b, \text{solvent}}$

Here  $\Delta T_b$  is directly proportional to molality of solution

$$\Delta T_b \propto m,$$

$$\Delta T_b = K_b m$$

If molality of the solution is one, then

$$\Delta T_b = K_b$$

The elevation in B.P. is also given as

$$\Delta T_b = K_b \times \frac{w}{M} \times \frac{1000}{W}$$

Molecular weight of solute can be find out as follows

$$M = \frac{K_b \times w \times 1000}{\Delta T_b \times W}$$

Here  $w$  = weight of solute

$W$  = weight of solvent

$K_b$  = molal elevation constant or ebullioscopic constant.

$M$  = molarmass of solute

$$K_b = \frac{RT^2}{1000 Lv \text{ or } \Delta Hv}.$$

Here  $Lv$  or  $\Delta Hv$  = latent heat of vapourization.

- If molar of molecular elevation in boiling point constant ( $K$ ) is used take 100 in place of 1000 that is,  $K$  is 10 times to that of  $K_b$

$$\Delta T_b = K \times \frac{w}{m_w} \times \frac{100}{W}$$

$$K = \frac{RT^2}{100 Lv}$$

## Illustrations

9. Calculate the boiling point of a solution containing 0.61 g of benzoic acid in 50 g of carbon disulphide assuming 84 % dimerisation of the acid. The boiling point and  $K_b$  of  $CS_2$  are  $46.2^\circ C$  and  $2.3 \text{ K kg mol}^{-1}$ .

**Solution**  $\Delta T = \frac{1000 \times K_b \times w}{m \times W}$

$$\Delta T_N = \frac{1000 \times 2.3 \times 0.61}{122 \times 50}$$

(molecular weight of  $C_6H_5COOH = 122$ )

$$\Delta T_N = 0.23$$

$$\Delta T_{\text{exp}} = \Delta T_N (1 - \alpha + \frac{\alpha}{n})$$

$$= 0.23 \times (1 - 0.84 + \frac{0.84}{2})$$

$$= 0.23 \times (1 - \frac{0.84}{2}) = 0.1334$$

$$\text{Boiling point} = 46.2 + 0.1334 = 46.3334^\circ C$$

## 9.12 ■ Solutions and Colligative Properties

10. Calculate the boiling point of a 5 % solution of cane sugar ( $C_{12}H_{22}O_{11}$ ). Molal elevation constant for water is  $0.52 \text{ K kg mol}^{-1}$ .

### Solution

$$w = 5 \text{ g}, W = 65 \text{ g}$$

$$m = 342, K_b = 0.52$$

$$\Delta T_b = \frac{K_b \times w \times 1000}{m \times W}$$

$$= \frac{0.52 \times 5 \times 1000}{342 \times 95} = 0.08 \text{ K}$$

$$\text{B.P. of solution, } T_1 = T_0 + \Delta T_b = 373 + 0.08$$

$$(\text{As } T_b = \text{B.P. of water} = 373 \text{ K}) = 373.08 \text{ K}$$

11. Calculate the elevation in boiling point when 12.5 g of urea is dissolved in 170 g of water. Molecular mass of urea is 60 and molal elevation constant of water is  $0.52 \text{ K kg mol}^{-1}$ .

### Solution

$$w = 12.5 \text{ g}$$

$$m = 60$$

$$W = 170 \text{ g}$$

$$K_b = 0.52 \text{ K kg mol}^{-1}$$

$$\Delta T_b = ?$$

$$\Delta T_b = \frac{K_b \times w \times 1000}{m \times W}$$

$$= \frac{12.5 \times 0.52 \times 1000}{60 \times 170} = 0.63 \text{ K}$$

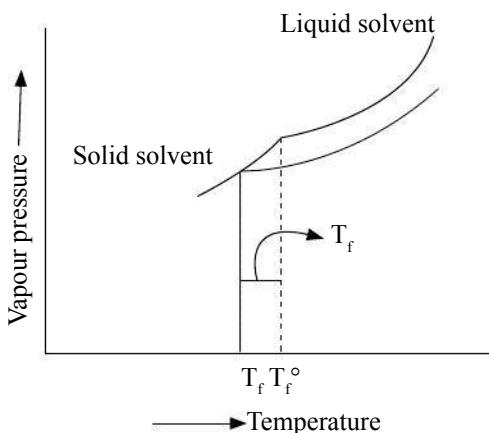
### Depression in Freezing Point

**Freezing Point:** It is the temperature at which the liquid and the solid form of the same substance are in equilibrium and have the same vapour pressure. A solution freezes when its vapour pressure is equal to the V.P. of pure solid solvent. Due to lower vapour pressure of the solution, solid form of a solution separates out at a lower temperature.

On adding a non-volatile solute to the solvent its vapour pressure decreases and becomes equal to the V.P. of solid solvent at lower temperature hence the freezing point of solvent also decreases.

Suppose  $T_f^o, T_f$  are the freezing point of pure solvent and solution respectively than decrease in freezing point  $\Delta T_f$  is given as

$$\Delta T_f = T_f^o - T_f$$



- This is also termed as cryoscopy and depression of freezing point ( $\Delta T_f$ ).
- It can be measured by Beckmann's thermometer method and Rast's method.
- For a dilute solution,  $\Delta T_f$  is directly proportional to the molality (m) of the solution.

$$\text{Hence } \Delta T_f \propto m$$

$$\Delta T_f = K_f m$$

If molality of the solution is one, then

$$\Delta T_f = K_f$$

$\Delta T_f$  and M can be found out by using these relations.

$$\Delta T_f = K_f \frac{w}{M} \times \frac{1000}{W}$$

$$M = \frac{K_f \times w \times 1000}{\Delta T_f \times W}$$

Here w = Weight of solute

$W$  = Weight of solvent

$K_f$  = Molal depression constant or cryoscopic constant

$M$  = Molar mass of Non-volatile solute.

$$K_f = \frac{RT^2}{1000 L_f \text{ or } \Delta H_{\text{fusion}}}.$$

Here  $L_f$  or  $\Delta H_f$  = latent heat of fusion.

- If molar of molecular depression in freezing point constant ( $K$ ) is used take 100 in place of 1000 that is,

$$K = 10 K_f$$

$$\Delta T_f = K \times \frac{w}{m_w} \times \frac{100}{W}$$

$$K = \frac{RT^2}{100 L_f}.$$

### REMEMBER

- The value of  $K_v$  or  $K_f$  depends on only nature of solvent and not on the nature of the solute.

### Illustrations

- How much ethyl alcohol must be added to 1.00 litre of water so that the solution will freeze at  $14^{\circ}\text{F}$ ? ( $K_f$  for water =  $1.86^{\circ}\text{C/mol}$ )

**Solution**  $\frac{F - 32}{9} = \frac{C}{5}$ .

$$\frac{14 - 32}{9} = \frac{C}{5}.$$

$$C = -10^{\circ}\text{C}$$

$$\Delta T = 10$$

$$\Delta T = K_f \times \text{molality}$$

$$10 = 1.86 \times \frac{w}{46 \times 1}.$$

$$w = 247.31 \text{ g}$$

- 1.4 g of acetone dissolved in 100 g of benzene gave a solution which freezes at  $277.12^{\circ}\text{K}$ . Pure benzene freezes at  $278.4^{\circ}\text{K}$ . 2.8 g of a solid (A) dissolved in 100 g of benzene gave a solution which froze at  $277.76^{\circ}\text{K}$ . Calculate the molecular weight of (A).

**Solution** For acetone + benzene mixture:

$$\Delta T = \frac{K_f \times 1000 \times w}{m \times W}$$

$$(278.40 - 277.12) = \frac{1000 \times K_f \times 1.4}{100 \times 58}$$

$$1.28 = \frac{1000 \times K_f \times 1.4}{100 \times 58} \quad \dots \dots \text{(i)}$$

For solute (A) + benzene mixture

Suppose  $m$  is the molecular weight of (A).

$$(278.40 - 277.76) = \frac{1000 \times m K_f \times 2.8}{100 \times m}$$

$$0.64 = \frac{1000 \times K_f \times 2.8}{100 \times m} \quad \dots \dots \text{(ii)}$$

From equation (i) and (ii), we get  $m = 232$

- The freezing point of a solution containing  $50 \text{ cm}^3$  of ethylene glycol in 50 g of water is found to be  $-34^{\circ}\text{C}$ . Assuming ideal behaviour, calculate the density of ethylene glycol ( $K_f$  for water =  $1.86 \text{ K Kg mol}^{-1}$ ).

**Solution** Ethylene glycol =  $50 \text{ cm}^3$

$$K_f = 1.86 \text{ K kg mol}^{-1}$$

$$\text{Mass of glycol (w)} = V \times d = 50 \times d \text{ g}$$

$$\text{Mass of water (W)} = 50 \text{ g}$$

$$\Delta T_f = 34^{\circ}\text{C}$$

$$\Delta T_f = \frac{K_f \times w \times 1000}{m \times W}$$

$$34 = \frac{1.86 \times 50 \times d \times 1000}{62 \times 50}$$

$$d = 1.133 \text{ g/cm}^3$$

## 9.14 ■ Solutions and Colligative Properties

15. Calculate the amount of ice that will separate out on cooling a solution containing 50 g of ethylene glycol in 200 g water to  $-9.3^{\circ}\text{C}$ . ( $K_f$  for water =  $1.86 \text{ K kg mol}^{-1}$ ).

**Solution**  $w = 50 \text{ g}$ ,  $\Delta T_f = 9.3$

$$K_f = 1.86 \text{ K kg mol}^{-1}$$

$$m = 62$$

$$W = ?$$

$$\Delta T_f = \frac{K_f \times w \times 1000}{m \times W}$$

$$9.3 = \frac{1.86 \times 62 \times W \times 1000}{62 \times W}$$

$$W = 161.29 \text{ g}$$

Hence amount of ice separated from 200 g water  
 $= 200 - 161.29 = 38.71 \text{ g}$ .

16. Find the freezing point of an aqueous solution of a non-electrolyte having an osmotic pressure of 2.0 atm at 300 K.

$$(K_f = 1.86 \text{ K kg mol}^{-1}, R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1})$$

**Solution**  $PV = nRT$

$$\frac{n}{V} = \frac{P}{RT} \cdot$$

$$= \frac{2 \text{ atm}}{0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}} \cdot$$

$$= 0.0812 \text{ mol L}^{-1}$$

$$\text{As } \Delta T_f = K_f \times \text{molality}$$

$$= 1.86 \text{ K kg mol}^{-1} \times 0.0812 \text{ mol L}^{-1}$$

$$= 0.151 \text{ K}$$

Freezing point of aqueous solution

$$= 273 - 0.151 = 272.849 \text{ K}$$

### Van't Hoff's Factor

Certain solutes, which undergo dissociation or association in solution, are found to show abnormal molecular mass. Due to it the colligative property

becomes abnormal which can be explained by Van't Hoff factor 'i'.

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$$

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

$$i = \frac{\text{Actual number of particles or species}}{\text{Expected number of particles or species}}$$

- For solutes showing neither dissociation nor association, the Van't Hoff's factor 'i' is 1.

Example, Urea, glucose, sucrose

- For solutes showing dissociation, the Van't Hoff's factor (i) is  $> 1$ .

Example,  $\text{FeCl}_3 \rightarrow \text{Fe}^{3+} + 3\text{Cl}^-$

Here  $i = 4$ .

$i=2$  for  $\text{NaX}$ ,  $\text{KX}$ ,  $\text{AgNO}_3$ ,  $\text{BaSO}_4$

$i=3$  for  $\text{Sr}_2$ ,  $\text{CaCl}_2$ ,  $\text{Na}_2\text{O}$

$i=4$  for  $\text{AlCl}_3$ ,  $\text{K}_3\text{Fe}(\text{CN})_6$

$i=5$  for  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{K}_4\text{Fe}(\text{CN})_6$

- Degree of dissociation ( $\alpha$ ) =  $\frac{i-1}{n-1}$

$$= \frac{M_t - M_o}{M_o} \left( \frac{1}{n-1} \right)$$

Here n is number of species formed after dissociation,  $M_o$ ,  $M_t$  are observed and theoretical molar mass respectively.

- For solutes showing association, the Van't Hoff's factor i  $< 1$ .

Example, In dimerization of acids like benzoic acid in benzene. (Due to HG-bonding)

- Degree of Association:

$$\alpha = \frac{n(1-i)}{n-1} = \frac{M_o - M_t}{M_o} \left( \frac{n}{n-1} \right)$$

Here n = Number of species formed after association.

- When dissociation occurs colligative properties increase while on association colligative properties decreases.

**REMEMBER**

$$\Delta T_b = i \cdot K_b M$$

$$\Delta T_f = i \cdot K_f M$$

$$\pi = i C RT$$

$$\frac{P - P_s}{P} = i \left[ \frac{n}{n + N} \right]$$

**Illustrations**

17. The freezing point of a solution containing 0.2 g of acetic acid in 20.0 g benzene is lowered by  $0.45^{\circ}\text{C}$ . Calculate the degree of association of acetic acid in benzene. Assume acetic acid dimerises in benzene.  $K_f$  for benzene = 5.12 K mol<sup>-1</sup> Kg.

**Solution** Given:

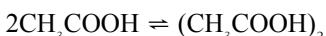
$$w = 0.2 \text{ g}, \quad W = 20 \text{ g},$$

$$\Delta T = 0.45^{\circ}\text{C}$$

$$\Delta T = \frac{1000 \times K_f \times w}{m \times W}$$

$$0.45 = \frac{1000 \times 5.12 \times 0.2}{20 \times m}$$

$$\text{So } m \text{ (observed)} = 113.78$$



$$\begin{array}{ccc} \text{Before association} & 1 & 0 \end{array}$$

$$\begin{array}{ccc} \text{After association} & (1 - \alpha) & \alpha/2 \end{array}$$

Here  $\alpha$  is the degree of association

$$\frac{m \text{ (normal)}}{m \text{ (observed)}} = 1 - \alpha + \frac{\alpha}{2}.$$

$$\frac{60}{113.78} = 1 - \alpha + \frac{\alpha}{2}.$$

$$\alpha = 0.945 \text{ or } 64.5 \%$$

18. 2 g of benzoic acid dissolved in 25 g of  $\text{C}_6\text{H}_6$  shows a depression in freezing point equal to

1.62 K. Molal depression constant of  $\text{C}_6\text{H}_6$  is 4.9 K mol<sup>-1</sup> kg. What is the percentage association of acid if it forms double molecule in solution?

**Solution** Given:

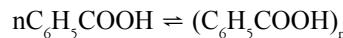
$$w = 2 \text{ g}, \quad W = 25 \text{ g}, \quad \Delta T = 1.62$$

$$K_f' = 4.9$$

$$\Delta T = \frac{1000 \times K_f' \times w}{m \times W}$$

$$1.62 = \frac{1000 \times 4.9 \times 2}{25 \times m}$$

$$m_{\text{exp}} = 241.98$$



$$\begin{array}{ccc} \text{Before association} & 1 & 0 \end{array}$$

$$\begin{array}{ccc} \text{After association} & (1 - \alpha) & \alpha/n \end{array}$$

Total number of mole at equilibrium

$$= 1 - \alpha + \frac{\alpha}{n}$$

$$\frac{m_N}{m_{\text{exp}}} = 1 - \alpha + \frac{\alpha}{n}.$$

$$\text{For dimer formation, } n = 2$$

$$\frac{122.0}{241.98} = 1 - \alpha + \frac{\alpha}{2}.$$

$$(m_N = 122.0 \text{ for } \text{C}_6\text{H}_5\text{COOH})$$

$$1 - \frac{\alpha}{2} = 0.504$$

$$\alpha = 0.992 \text{ or } 99.2 \%$$

19. A 1.2 % solution (weight/volume) of NaCl is isotonic with 7.2% solution (weight/volume) of glucose. Calculate degree of ionization and Van't Hoff factor of NaCl.

**Solution**  $\% \text{ of wt/volume} = \frac{\text{Wt. of solute}}{\text{Volume of solution}} \times 100$

$$\text{Weight of glucose} = 7.2 \text{ g}$$

$$\text{Volume of solution} = 100 \text{ ml}$$

## 9.16 ■ Solutions and Colligative Properties

For glucose:

$$\pi_{\text{exp}} \text{ or } \pi_N = \frac{W}{m \times V \times ST}$$

$$= \frac{7.2 \times 1000 \times 0.0821 \times T}{180 \times 100}$$

For NaCl:

$$\pi_N = \frac{W}{m \times V \times ST}$$

$$= \frac{1.2 \times 1000 \times 0.0821 \times T}{58.5 \times 100}$$

As both the solutions are isotonic so,

$$\pi_{\text{exp}} (\text{NaCl}) = \pi_N (\text{Glucose})$$

For NaCl

$$\frac{\pi_{\text{exp}}}{\pi_N} = 1 + \alpha$$

$$(7.2 \times 1000 \times 0.0821 \times T) / (180 \times 100)$$

$$\times (58.5 \times 100) / (1.2 \times 1000 \times 0.0821 \times T)$$

$$= 1 + \alpha = (i)$$

$$\alpha = 0.95$$

$$i = 1.95$$

- 20.** Assuming complete dissociation, calculate the expected freezing point of a solution prepared by dissolving 6.00 g of Glauber's salt,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  in 0.100 kg of  $\text{H}_2\text{O}$ . (Given for water,  $K_f = 1.86 \text{ K kg mol}^{-1}$ , Atomic masses: Na = 23, S = 32, O = 16, H = 1).

**Solution** Molecular mass of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

$$= (2 \times 23) + 32 + (16 \times 4) + (10 \times 18)$$

$$= 322 \text{ g/mol}$$



$$\text{Van't Hoff factor (i)} = 2 + 1 = 3$$

$10\text{H}_2\text{O}$  molecules are not considered for calculating Van't Hoff factor because water is solvent.

$$\text{Molality} = \frac{\text{Moles of Glauber salt}}{\text{Mass of solvent in kg}}$$

$$= \frac{6 \text{ g}}{322 \text{ g/mol}} \times \frac{1}{0.1 \text{ kg}}$$

$$T_0 - T_f = \Delta T_f = i \cdot K_f \cdot m$$

$$= 3 \times 1.86 \times \frac{6}{322 \times 0.1} = 1.04 \text{ K}$$

$$T_f = T - 1.04$$

$$= 273 - 1.04 = 271.96 \text{ K}$$

- 21.** X g of a non-electrolyte compound (molar mass = 200) are dissolved in 1.0 litre of 0.05 M NaCl aqueous solution. The osmotic pressure of this solution is found to be 4.92 atm at 27°C. Calculate the value of X. Assume complete dissociation of NaCl and ideal behaviour of this solution. ( $R = 0.082 \text{ litre atm mol}^{-1} \text{ K}^{-1}$ ).

**Solution** Given:

$$\pi = 4.92 \text{ atm}; T = 27 + 273 = 300 \text{ K}$$

$$V = 1 \text{ litre}$$

$$n_1 = \text{mole of non-electrolyte} = \frac{X}{200}$$

$$n_2 = \text{mole of NaCl} = 0.05$$

$$\text{According to } \pi V = n ST$$

$$\pi V = n_1 ST + n_2 (1 + \alpha) ST$$

$$\pi V = [n_1 + n_2 (1 + \alpha)] ST;$$

Here  $\alpha = 1$  given for NaCl

$$4.92 \times 1 = [( \frac{X}{200} ) + 0.05 \times 2] \times 0.082 \times 300$$

$$X = 20 \text{ g.}$$

- 22.** 0.85 % aqueous solution of  $\text{NaNO}_3$  is apparently 90% dissociated at 27°C. Calculate its osmotic pressure. ( $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$ )

**Solution**

	$\text{NaNO}_3$	$\rightleftharpoons$	$\text{Na}^+$	$+$	$\text{NO}_3^-$
Initial	1 mol		0		0
Equilibrium	$m(1 - 0.9)$		0.9 M		0.9 M

Total particles after dissociation

$$= 1 - 0.9 + 0.9 + 0.9 = 1.9$$

Initial moles of  $\text{NaNO}_3$

$$\begin{aligned} \text{Mass of } \text{NaNO}_3 \text{ in 10 ml solution} \\ = \frac{\text{Molecular mass of } \text{NaNO}_3}{\text{Molecular mass of } \text{NaNO}_3} \\ = \frac{0.85}{85} = 0.01 \text{ mol} \end{aligned}$$

Total moles of particles after dissociation

$$= 0.01 \times 1.9 = 0.019 \text{ m}$$

$$\pi V = nRT$$

$$\pi = \frac{nRT}{V}.$$

$$= \frac{0.019 \times 0.082 \times 300}{(100/1000 \text{ L})} = 4.674 \text{ atm.}$$

23. A 0.15 molar solution of phenol in water gave an osmotic pressure of 2.82 atm at 27°C. Calculate the Vant Hoff's factor. If phenol forms double molecules in solution, calculate the degree of association.

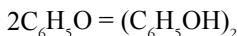
**Solution** As theoretical osmotic pressure ( $\pi_c$ ) =  $c RT$

$$= 0.15 \times 0.0820 \times 300 = 3.69 \text{ atm}$$

Observed osmotic pressure ( $\pi_o$ ) = 2.82 atm

$$\text{Vant Hoff factor (i)} = \frac{\pi_o}{\pi_c} = \frac{2.82}{3.69} = 0.7633$$

The low value observed for osmotic pressure suggests that phenol molecules in water have undergone association.



$$1 - \alpha \alpha/2$$

Here  $\alpha$  is the degree of association.

Total number of moles after association

$$= 1 - (-\alpha) + \frac{\alpha}{2} = (1 - \frac{\alpha}{2}) \text{ moles}$$

Number of moles if no association occurs = 1 mole

$i = \frac{\text{Total moles after association}}{\text{No. of moles when there is no association}}$

$$0.7633 = \left(\frac{1 - \alpha/2}{1}\right)$$

$$0.7633 = \left(1 - \frac{\alpha}{2}\right)$$

$$\alpha = 0.4734$$

$$= 47.34 \%$$

## Enhance Your Knowledge

### Osmosis

- Osmosis was first observed by Abbe Nollet in 1748. In osmosis there is a net flow of solvent molecules from the solvent to the solution or from a less concentrated solution to a more concentrated solution through a semi permeable membrane (animal membrane, cell wall,  $\text{Ca}_3(\text{PO}_4)_2$ , Copper ferrocyanide  $[\text{Cu}_2\text{Fe}(\text{CN})_6]$ ).
- Plant and trees absorb water from soil by osmosis.
- In osmosis, semi-permeable membrane is required but not in diffusion. In diffusion, flow is from higher to lower concentration.

### Osmotic Pressure

It is the equilibrium hydrostatic pressure of the column set up as a result of osmosis, Or, It is the minimum pressure that must be applied on the solution to prevent the entry of the solvent into the solution through the semi permeable membrane. Or It is the minimum pressure needed to apply on a solution to make its vapour pressure equal to be vapour pressure of solvent.

- It is denoted by P or  $\pi$ . It is measured by Pfeffer's method, Berkely-Hartley's method, Townsend's method etc. Townsend method is used to find osmotic pressure of non aqueous solution without using semi permeable membrane.
- **Van't Hoff's Equation of Osmotic Pressure:** It is as follows:

## 9.18 ■ Solutions and Colligative Properties

$$\pi = CST$$

Here  $\pi$  = osmotic pressure

C = concentration of solution in mol/lit

S or R = solution constant

( $\approx 0.0821$  lit-atm/deg-mol)

T = absolute temperature in K

So  $\pi \propto C$  (at constant temperature)

$$\pi = \frac{n}{V} ST \quad (C = n/V)$$

$$\pi V = nST$$

Here n = moles of solute,

V = volume of solution

$$\pi V = \frac{w}{M} RT$$

As  $n = w/M$

M = molar mass of solute

w = gram weight of solute

### ■ Determination of Molecular Weight from Osmotic Pressure

$$\frac{M}{W} = \frac{ST}{\pi}$$

$$M = \frac{WST}{\pi}$$

$$\pi V = nST \quad (n = W/M)$$

### ■ When solute is not dissolved in one litre or it is dissolved in V litre then

$$\pi V = \frac{W}{M} ST$$

$$M = \frac{W \times ST}{\pi \times V}$$

■ Accurate molecular weight is obtained in following conditions:

(i) Solution must be very dilute,

(ii) Solute must be non-volatile

(iii) Solute should not undergo dissociation or association in the solution.

■ **Isotonic Solution** Solutions having equal molar concentrations or equal osmotic pressures are called isotonic solutions. Example, 0.91 % solution of pure aqueous NaCl is isotonic with human RBC,

■ 6% urea and 0.1 M glucose are isotonic.

$$P_1 = P_2 \text{ or } \pi_1 = \pi_2$$

$$\frac{W_1}{M_1 V_1} = \frac{W_2}{M_2 V_2}$$

■ In isotonic solution net osmosis is not possible.

**Molecular Masses of Polymers:** It is best determined by osmotic pressure method firstly as other colligative properties give so low values that they cannot be measured accurately and secondly, osmotic pressure measurements can be made at room temperature and do not require heating which may change the nature of the polymer.

■ In a mixture of two solutions, the solution with lower osmotic pressure is Hypotonic while solution with higher osmotic pressure is Hypertonic. Here osmosis can take place.

■ At freezing point solid and liquid are in equilibrium so have vapour pressure.

■ On cooling solution at freezing point the crystals of solvent are separated first.

### Solved Problems from the IITs

- The vapour pressure of benzene at a certain temperature is 640 mm of Hg. A non volatile and non electrolyte solid weighing 2.175 g is added to 39.08 g of benzene. The vapour pressure of the solution is 600 mm of Hg. What is the molecular weight of solid substance?

[IIT 1990, MLNR 1992]

$$p \text{ for benzene} = 640 \text{ mm}$$

$$ps \text{ for solution} = 600 \text{ mm}$$

$$\text{Weight of non-volatile and non-electrolyte solute (w)} = 2.175 \text{ g}$$

$$\text{Weight of solvent (benzene)} = 39.0 \text{ g}$$

Mol. wt. of benzene (M) =  $72 + 6 = 78$

Mol. wt. of non-volatile and non-electrolyte solute (m) = ?

$$\frac{p - ps}{p} = \frac{w}{W} \times M$$

$$m \times W$$

$$\frac{640 - 600}{640} = \frac{2.175 \times 78}{m \times 39}$$

$$m = 69.60$$

2. Calculate the molality of one litre solution of 93%  $H_2SO_4$  (weight/volume). The density of solution is 1.84 g/ml.

[IIT 1990]

93 %  $H_2SO_4$  solution (weight/volume) means that 100 ml solution contains = 93 g of  $H_2SO_4$ .

Hence, in 1000 ml solution contains = 930 g of  $H_2SO_4$

Weight = volume  $\times$  density

$$1000 \times 1.84 = 1840 \text{ g solution contains}$$

$$= 930 \text{ g of } H_2SO_4$$

In this solution, weight of solvent

$$= 1840 - 930$$

$$= 910 \text{ g} = 0.910 \text{ kg}$$

Molality of  $H_2SO_4$  solution

$$= \frac{\text{Wt. of } H_2SO_4 / \text{mol. wt. of } H_2SO_4}{\text{Wt. of solvent in kg}}$$

$$= \frac{930/98}{0.910} = 10.428 \text{ m}$$

3. The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. A non-volatile non-electrolyte solid weighting 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular mass of the solid substance?

[IIT 1990]

According to Raoult's law,

$$M_B = \frac{w \times M}{W} \times \frac{P_A^o}{P_A^o - P_A}$$

$$w = 2.175 \text{ g}, W = 39.0 \text{ g}$$

$$M = 78, m = ?$$

$$P_A^o = 640 \text{ mm of Hg}$$

$$P_A = 600 \text{ mm of Hg}$$

$$m = \frac{2.175 \times 78}{39.0} \times \frac{600}{640 - 600} \\ = \frac{2.175 \times 78}{39.0} \times \frac{600}{40} = 65.25$$

4. The degree of dissociation of  $Ca(NO_3)_3$  in a dilute aqueous solution, containing 7.0 g of the salt per 100 g of solution at  $100^\circ C$  is 70 per cent. If the vapour pressure of water at  $100^\circ C$  is 760 mm, calculate the vapour pressure of the solution.

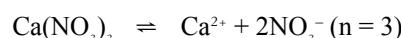
[IIT 1991]

**Solution**  $\Delta p_{\text{theo}} = \text{Lowering in vapour pressure}$  when there is no dissociation

$$\Delta p_{\text{theo}} = p_0 \times \frac{w \times M}{W \times m}$$

$$= \frac{760 \times 14 \times 18}{200 \times 164} = 5.84 \text{ mm}$$

$$\text{Degree of dissociation} = \frac{70}{100} = 0.7$$



$$\frac{\Delta p_{\text{obs.}}}{\Delta p_{\text{theo}}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles when there is no dissociation}}$$

$$= \frac{1 + (n - 1)\alpha}{1} = \frac{1 + (3 - 1) \times 0.7}{1} = 2.4$$

$$\text{So } \Delta p_{\text{obs.}} = 2.4 \times \Delta p_{\text{theo}} = 2.4 \times 5.84 = 14.02 \text{ mm}$$

$$p_0 - p_s = \Delta p_{\text{obs.}} = 14.02$$

$$p_s = p_0 - 14.02$$

$$= 760 - 14.02 = 745.98 \text{ mm}$$

5. Addition of 0.643 g of a compound to 50 ml of benzene (density = 0.879 g/mL) lowers the freezing point from  $5.51^\circ C$  to  $5.03^\circ C$ . If  $K_f$  for benzene is 5.12, calculate the molecular weight of the compound.

[IIT 1990]

## 9.20 ■ Solutions and Colligative Properties

**Solution** Molality of the solution

$$= \frac{\Delta T_f}{K_f} = \frac{0.48}{5.12} = 0.09375$$

$$\frac{0.643/M}{(50 \times 0.879/1000)} = 0.09375$$

$$M = \frac{0.643 \times 1000}{50 \times 0.879 \times 0.09375} .$$

$$= 156.06 \text{ g mol}^{-1}$$

6. Addition of 0.643 g of a compound to 50 ml of benzene (density = 0.879 g/ml) lowers the freezing point from 5.51°C to 5.03°C. If  $K_f$  for benzene is 5.12, calculate the molecular weight of the compound.

[IIT 1992]

$$K_f = 5.12 \text{ K kg mol}^{-1}$$

$$w = 0.643 \text{ g}$$

$$\Delta T_f = T_0 - T_1 = 5.51 - 5.03 = 0.48$$

$$W = 43.95 \text{ (m = v} \times d = 50 \text{ ml} \times 0.879)$$

$$m = ?$$

$$m = \frac{K_f \times w \times 1000}{\Delta T_f \times W}$$

$$= \frac{5.12 \times 0.643 \times 1000}{0.48 \times 43.95}$$

$$= 156.$$

7. What mass of non volatile solute (urea) needs to be dissolved in 100 g of water in order to decrease the vapour pressure of water by 25%. What will be the molality of solution?

**Solution** According to Raoult's law

$$\frac{P_0 - P_s}{P_s} = \frac{w \times M}{W \times m}$$

$$\text{If } P_0 = 100 \text{ mm and } P_s = 75 \text{ mm}$$

$$\frac{100 - 75}{75} = \frac{w \times 18}{100 \times 60} .$$

$$w = 111.1$$

$$\text{Molality} = \frac{w \times 1000}{m \times W}$$

$$= \frac{111.1 \times 1000}{60 \times 100} = 18.52 \text{ m}$$

8.  $8.0575 \times 10^{-2}$  kg of Glauber's salt is dissolved in water to obtain 1 dm<sup>3</sup> of a solution of density 1077.2 kg m<sup>-3</sup>. Calculate the molarity, molality and mole fraction of Na<sub>2</sub>SO<sub>4</sub> in the solution.

[IIT 1994]

$$\text{Volume of solution} = 1 \text{ dm}^3$$

$$\text{Density} = 1077.2 \text{ kg m}^{-3}$$

$$\text{Mass of Na}_2\text{SO}_4 = 1077.2 - 1000$$

$$= 77.2 \text{ g in 1 litre of solution}$$

$$\text{Moles of Na}_2\text{SO}_4 = \frac{77.2}{142} = 0.5436$$

$$\text{Molarity} = 0.5436 \text{ M}$$

$$\text{Molality} = 0.5436 \text{ m}$$

$$\text{Mole fraction} = \frac{0.5436}{0.5436 + 55.55} = 0.0096$$

9. The molar volume of liquid benzene (density = 0.877 g mL<sup>-1</sup>) increases by a factor of 2750 as it vaporizes at 20°C and that of liquid toluene (density = 0.867 g mL<sup>-1</sup>) increases by a factor of 7720 at 20°C. A solution of benzene and toluene at 20°C has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution.

[IIT 1996]

**Solution** For benzene

In vapour phase

1 mole that is, 78 g benzene has volume at 293 K

$$= \frac{78 \times 1}{0.877} \times 2750 \text{ mL}$$

Similarly, 1 mole of 92 g toluene has volume at 293 K

$$= \frac{92 \times 1}{0.867} \times 7720 \text{ mL}$$

$$\text{As } PV = nRT$$

$$\text{So } \frac{P_B^o}{760} \times \frac{7 \times 2750}{0.877 \times 1000} = 1 \times 0.0821 \times 293$$

$$P_B^o = 74.74 \text{ mm}$$

Similarly, for toluene

$$\frac{P_{\text{T}}^{\circ}}{760} \times \frac{92 \times 7720}{0.867 \times 1000} = 1 \times 0.0821 \times 293$$

$$P_{\text{T}}^{\circ} = 22.37 \text{ mm}$$

$$\text{As } P_m = P_{\text{B}}^{\circ} X_{\text{B}} + P_{\text{T}}^{\circ} X_{\text{T}}$$

$$P_m = P_{\text{B}}^{\circ} X_{\text{B}} + P_{\text{T}}^{\circ} (1 - X_{\text{B}})$$

$$46 = 74.74 X_{\text{B}} + 22.37 (1 - X_{\text{B}})$$

$$\text{Hence } X_{\text{B}} = 0.45 \quad (\text{In liquid phase})$$

$$\text{As } X_{\text{B}} + X_{\text{T}} = 1$$

$$\text{So } X_{\text{T}} = 0.55 \quad (\text{In liquid phase})$$

$$\text{As } P'_{\text{B}} = P_{\text{B}}^{\circ} \cdot X_{\text{B}} = P_m \cdot X'_{\text{B}}$$

$$\text{that is, } 74.74 \times 0.45 = 46 \times X'_{\text{B}}$$

$$\text{So } X'_{\text{B}} \text{ (In gas phase)} = 0.73$$

10. A very small amount of a non volatile solute (that does not dissociate) is dissolved in 56.8 cm<sup>3</sup> of benzene (density = 0.889 g cm<sup>-3</sup>) . At room temperature vapour pressure of this solution is 98.88 mm Hg while that of benzene is 100 mm Hg. Calculate the molality of this solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene, what is the value of molal freezing point depression constant of benzene?

[IIT 1997]

**Solution** According to Raoult's law,

$$\frac{P - P_s}{P} = \frac{n}{N}.$$

$$\frac{100 - 98.8}{100} = \frac{n}{1000 / 78}.$$

$$\frac{1.12}{100} = \frac{78 \times n}{1000}$$

$$n = \frac{1.12 \times 1000}{100 \times 78}$$

$$= 0.144 \text{ m}$$

$$\Delta T_f = K_f \times \text{molality}$$

$$0.73 = K_f \times 0.144$$

$$K_f = \frac{0.73}{0.144} = 5.07 \text{ K kg mol}^{-1}$$

11. A 6.90 M solution of KOH in water contains 30% by weight of KOH. What is the density of the solution?

[IIT 1997]

**Solution** Molarity of KOH solution = 6.90 M

$$\text{Mol. wt. of KOH} = 39 + 16 + 1 = 56$$

$$\text{Weight of KOH in one litre solution}$$

$$= \text{Molarity} \times \text{mol. wt}$$

$$= 6.90 \times 56 = 386.4 \text{ g.}$$

Since the solution of KOH is 30% it means that 30 g of KOH are present in

$$\frac{100}{30} \times 386.4 \text{ g of solution}$$

$$= 1288 \text{ g of solution}$$

$$\text{Density} = \frac{\text{Weight in g}}{\text{Volume in ml}} = \frac{1288 \text{ g}}{1000 \text{ ml}}.$$

$$= 1.288 \text{ g ml}^{-1}$$

12. A solution of a non-volatile solute in water freezes at -0.30°C. The vapour pressure of pure water at 298 K is 23.51 mm Hg and K<sub>f</sub> for water is 1.86 degree/molal. Calculate the vapour pressure of this solution at 298 K.

[IIT 1998]

**Solution**  $\Delta T_f = K_f \times m$

According to Raoult's law,

$$\frac{P_A^{\circ} - P_A}{P_A} = \frac{w \times M}{m \times W} = \frac{w \times 1000 \times M}{m \times W \times 1000}.$$

$$\frac{P_A^{\circ} - P_A}{P_A} = m \text{ (molality)} \times \frac{M}{1000}.$$

$$\frac{P_A^{\circ} - P_A}{P_A} = \frac{\Delta T_f}{K_f} \times \frac{M}{1000}.$$

## 9.22 ■ Solutions and Colligative Properties

$$P_A^o = 23.51 \text{ mm Hg}$$

$$K_f = 1.86 \text{ K/molal}$$

$$M = 18$$

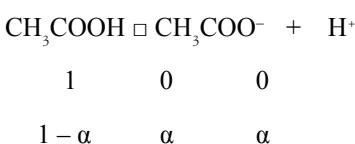
$$\frac{23.51 - P_A}{P_A} = \frac{0.3}{1.86} \times \frac{18}{1000} = 23.44 \text{ mm Hg}$$

13. To  $500 \text{ cm}^3$  of water,  $3.0 \times 10^{-3} \text{ kg}$  acetic acid is added. If 23 % of acetic acid is dissociated, what will be the depression in freezing point?  $K_f$  and density of water are  $1.86 \text{ K kg mol}^{-1}$  and  $0.997 \text{ g cm}^{-3}$  respectively.

[IIT 2000]

**Solution**  $\Delta T_f = K_f \times \text{molality} \times (1 + \alpha)$

for  $\text{CH}_3\text{COOH}$



$$\text{As } \alpha = 23\% = 0.23,$$

$$\text{Molality} = \frac{\text{mol of CH}_3\text{COOH}}{\text{mass of water in kg.}}$$

$$= \frac{3.0 \times 10^{-3} \times 1000}{60 \times 500 \times 0.997} = 0.10$$

$$\Delta T_f = 1.86 \times 0.1 \times 1.23 = 0.288 \text{ K}$$

14. The vapour pressure of two miscible liquids (A) and (B) are 300 and 500 mm of Hg respectively. In a flask 10 mole of (A) is mixed with 12 mole of (B). However, as soon as (B) is added, (A) starts polymerizing into a completely insoluble solid. The polymerization follows first order kinetics. After 100 minute, 0.525 mole of a solute is dissolved which arrests the polymerization completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerization reaction. Assume negligible volume change on mixing and polymerization and ideal behaviour for the final solution.

[IIT 2001]

**Solution**  $A(l) + B(l) \rightarrow (A)_n + B(l)$

Insoluble

$$\text{As } P_m = P_A^o X_A + P_B^o X_B$$

$$\text{So } P_m = 300 \left( \frac{a}{12+a} \right) + 500 \left( \frac{12}{12+a} \right)$$

Here a mole of A are left after polymerization after 100 minute.

$$\text{As } K = \frac{2.303}{T} \log_{10} \frac{10}{a}$$

$$\text{So } K = \frac{2.303}{100} \log_{10} \frac{10}{a} \quad \dots \text{(ii)}$$

After 100 minutes polymerisation is checked.

After 100 minute solute is added and final vapour pressure is 400.

$$\text{So } \frac{P_m - 400}{400} = \frac{0.525}{(a + 12)} \quad \dots \text{(iii)}$$

After solving equation (i) and (ii)

$$a = 9.9 \quad \dots \text{(iv)}$$

On Putting the value of 'a' in equation (ii)

$$K = \frac{2.303}{100} \log_{10} \frac{10}{9.9}.$$

$$K = 1.0 \times 10^{-4}$$

15. Match the boiling point with  $K_b$  for X, Y and Z, if molecular weight of X, Y and Z are same.

	Boiling point	$K_b$
X	100	0.68
Y	27	0.53
Z	253	0.98

[IIT 2003]

**Solution** As  $K_b = \frac{RT_b^2}{1000 L_v}$ .

$$= \frac{RT_b^2 \cdot M}{1000 \Delta H_v} = \frac{RT_b \cdot M}{1000 \Delta S_v}.$$

$$\text{Also } \Delta S_v = \frac{\Delta H_v}{T_b}.$$

As during vaporization, entropy increases because randomness increases.  $\Delta S_v$  may be taken as almost constant as for, liquid  $\rightleftharpoons$  vapour even if the extent of disorderness varies from liquid to liquid because the  $S_v$  is abnormally higher than  $S_v - S_L = \Delta S_v$  is almost constant. If M and R are constant  $K_b \propto T_b$ .

$$\text{i.e., } K_b(X) = 0.68$$

$$K_b(Y) = 0.53$$

$$K_b(Z) = 0.98.$$

16. 1.22 g of benzoic acid is dissolved in (i) 100 g acetone ( $K_b$  for acetone = 1.7) and (ii) 100 g benzene ( $K_b$  for benzene = 2.6). The elevation in boiling points  $\Delta T_b$  is 0.17°C and 0.13°C respectively.

- (a) What are the molecular weights of benzoic acid in both the solutions?
- (b) What do you deduce out of it in terms of structure of benzoic acid?

IIT Mains 2004]

### Solution

- (a) If  $M_1$  = molecular mass of benzoic acid in acetone

$$\text{So } M_1 = \frac{K_b \times w_{\text{solute}} \times 1000}{\Delta T_b \times W_{\text{solvent}}}$$

$$= \frac{1.7 \times 1.22 \times 10000}{17 \times 100 \text{ g}} = 122 \text{ g/mol}$$

If  $M_2$  = molecular mass of benzoic acid in benzene.

$$M_2 = \frac{2.6 \times 1.22 \times 1000}{0.13 \times 100 \text{ g}} = 244 \text{ g/mol}$$

$$(b) i = \frac{\text{Normal molecular mass of benzoic acid}}{\text{Abnormal molecular mass of benzoic acid}}$$

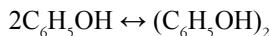
$$= \frac{122 \text{ g/mol}}{244 \text{ g/mol}}$$

$$= 0.5$$

This indicates that benzoic acid exists as dimer in benzene.

17. 75.2 g of  $C_6H_5OH$  (phenol) is dissolved in a solvent of  $K_f = 14$ . If the depression in freezing point is 7 K then find the % of phenol that dimerizes.

[IIT 2006]



$$7 = 14 \times 0.8 (2 - \alpha/2)$$

$$\alpha = 0.75 = 75 \%$$

## MULTIPLE-CHOICE QUESTIONS

### Straight Objective Type Questions (Single Choice only)

1. For which case would  $\Delta H_{\text{sol}}$  be expected to be negative?
  - (a) If solute-solvent interactions are the same as solvent-solvent and solute-solute interactions
  - (b) If solute-solvent interactions are much greater than solvent-solvent and solute-solute interactions
  - (c) If solute-solute interactions are much greater than solvent-solvent and solute-solvent interactions
  - (d) If solvent-solvent interactions are much greater than solute-solvent and solute-solute interactions
2. A liquid is in equilibrium with its vapour at its boiling point. On the average, the molecules in the two phase have equal
  - (a) intermolecular forces
  - (b) potential energy
  - (c) temperature
  - (d) kinetic energy
3. A molal solution is one that contains one mole of a solute in
  - (a) 1000 g of the solvent
  - (b) one litre of solvent
  - (c) one litre of solution
  - (d) 22.4 litre of the solution
4. Osmotic pressure of a solution is 0.0821 atm at a temperature of 300 K. The concentration in mole/lit will be
  - (a) 0.33
  - (b) 0.066
  - (c)  $0.3 \times 10^{-2}$
  - (d) 3
5. When mercuric iodide is added to the aqueous solution of potassium iodide, the
  - (a) freezing point is raised
  - (b) freezing point does not change
  - (c) freezing point is lowered
  - (d) boiling point does not change
6. A sugar syrup of weight 214.2 g contains 34.2 g of water. The molal concentration is

- (a) 0.55
- (b) 5.5
- (c) 55
- (d) 0.1
7. The depression in f.p. of 0.01 m aqueous solution of urea, sodium chloride and sodium sulphate is in the ratio
  - (a) 1 : 1 : 1
  - (b) 1 : 2 : 3
  - (c) 1 : 2 : 4
  - (d) 2 : 2 : 3
8. The freezing point of equimolar aqueous solution will be highest for
  - (a)  $C_6H_5N^+H_3Cl^-$  (aniline hydrochloride)
  - (b)  $Ca(NO_3)_2$
  - (c)  $La(NO_3)_3$
  - (d)  $C_6H_{12}O_6$  (Glucose)
9. The molal elevation constant of water is 0.51. The boiling point of 0.1 molal aqueous NaCl solution is nearly
  - (a) 100.05°C
  - (b) 100.1°C
  - (c) 100.2°
  - (d) 101.0C
10. Which of the following solutions will have the lowest freezing point?
  - (a) 0.0100 m  $Li_2SO_4$
  - (b) 0.015 m  $CaCl_2$
  - (c) 0.0100 m KCl
  - (d) 0.035 m  $CH_3CH_2CH_2OH$
11. Total vapour pressure of mixture of 1 mol X ( $P^o_X = 145$  torr) and 2 mol Y ( $P^o_Y = 245$  torr) is 200 torr. In this case:
  - (a) There is a negative deviation from Raoult's law
  - (b) There is a positive deviation from Raoult's law
  - (c) There is no deviation from Raoult's law
  - (d) Cannot be decided
12. On freezing an aqueous solution of sodium chloride, the solid that starts separating out is
  - (a) ice
  - (b) sodium chloride
  - (c) solution
  - (d) none of these
13. How many moles of  $Fe^{2+}$  ions are formed when excess iron is treated with 500 mL of 0.4 N HCl under inert atmosphere? Assume no change in volume.

- 14.** The vapour pressure of a solution of 5g of non electrolyte in 100 g of water at a particular temperature is  $2985 \text{ Nm}^{-2}$ . The vapour pressure of pure water at that temperature is  $3000 \text{ Nm}^{-2}$ . The molecular weight of the solute is

  - 180
  - 90
  - 270
  - 360

**15.** A solution obtained by dissolving 0.2 gm of solute in  $100 \text{ cm}^3$  of solution in benzene at  $21^\circ\text{C}$  develops a rise of 2.4 mm osmotic equilibrium. Find molarity and molality in the solution (If density of solution is  $0.88 \text{ gm/cm}^3$ ).

  - $8.3 \times 10^{-3} \text{ mol/L}$
  - $4.15 \times 10^{-6} \text{ mol/L}$
  - $8.3 \times 10^{-4}$
  - none

**16.** An aqueous solution containing 1 gm of urea boils at  $100.25^\circ\text{C}$ . The aqueous solution containing 3 gm of glucose in the same volume will boil at

  - $100.75^\circ\text{C}$
  - $100.5^\circ\text{C}$
  - $100^\circ\text{C}$
  - $100.25^\circ\text{C}$

**17.** Increasing the temperature of an aqueous solution will cause

  - decrease in molality
  - decrease in molarity
  - decrease in mole fraction
  - decrease in % (w/w).

**18.** Lowering of vapour pressure,  $\Delta p$ ; elevation in boiling point  $\Delta T_b$ ; and depression freezing point  $\Delta T_f$  of a solvent for the same molar concentration of each of the three solutes: (A) sugar, (B) NaCl and (C)  $\text{BaCl}_2$  following the sequence

  - $\Delta T_b : C > B > A$
  - $\Delta T_f : A < B < C$
  - $\Delta p : A < B < C$
  - All the above

**19.** The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to

  - ionization of benzoic acid

**20.** The osmotic pressure of a solution containing 4.0 g of solute (molar mass 246) per litre at  $27^\circ\text{C}$  is ( $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$ ).

  - 0.1 atm
  - 0.3 atm
  - 0.4 atm
  - 0.9 atm

**21.** The vapour pressure of a solvent A is 0.80 atm. When a non-volatile substance B is added to this solvent, its vapour pressure drops to 0.6 atm. The mole fraction of B in the solution is

  - 0.50
  - 0.25
  - 0.75
  - 0.95

**22.** People add sodium chloride to water while boiling eggs. This is to

  - decrease the boiling point
  - increase the boiling point
  - prevent breaking of eggs
  - make eggs tasty

**23.** Which of the following pairs of solutions have roughly the same boiling point elevation?

  - 0.100 m KCl and 0.0500 m  $\text{MgBr}_2$
  - 0.200 m NaCl and 0.300m  $\text{Na}^2\text{SO}_4$
  - 0.100 m  $\text{C}_6\text{H}_{12}\text{O}_6$  and 0.0333 m CuCl<sub>2</sub>
  - 0.100 m NaCl and 0.100 m  $\text{C}_6\text{H}_{12}\text{O}_6$

**24.** A solution of 1 molal concentration of a solute will have maximum boiling point elevation when the solvent is

  - Chloroform
  - Benzene
  - Ethyl alcohol
  - Acetone

**25.** The depression in freezing point for 1 M urea, 1 M glucose and 1 M NaCl are in the ratio

  - 1 : 2 : 3
  - 1 : 1 : 2
  - 3 : 2 : 1
  - 1 : 2 : 1

**26.** The beans are cooked earlier in pressure cooker, because

  - boiling point increase with increasing pressure
  - boiling point decrease with increasing pressure
  - extra pressure of pressure cooker, softens the beans

### **9.26 ■ Solutions and Colligative Properties**



### 9.28 ■ Solutions and Colligative Properties

- (a)  $-1.12\text{ K}$       (b)  $0.56\text{ K}$   
 (c)  $1.12\text{ K}$       (d)  $-0.56\text{ K}$
67. Phenol dimerizes in benzene having Van't Hoff factor 0.54. What is the degree of association?  
 (a) 0.45      (b) 0.92  
 (c) 46      (d) 92
68. In the solubility of liquid solutions  
 (a) a positive heat of solution means heat is absorbed as the solute dissolves to form the saturated solution  
 (b) a positive enthalpy of solutions is when the system gains thermal energy on becoming saturated at the fixed temperature  
 (c) there is no noticeable temperature changes  
 (d) the solubility of a solute always increases with increasing temperature
69. What characteristics must a slightly soluble salt have if it is to be dissolved in water by increasing the temperature?  
 (a) A smaller value for  $K_{sp}$  at the higher temperature  
 (b) A high negative slope for the solubility curve  
 (c) A low positive slope for the solubility curve  
 (d) A high positive slope for the solubility curve
70. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. The vapour pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be  
 (a) 300      (b) 700  
 (c) 360      (d) 350
71. The relative lowering of vapour pressure produced by a solution of 18 g of urea in 100 g of water is approximately  
 (a) 0.025      (b) 0.5  
 (c) 0.05      (d) 0.25
72. A 5.25 % solution of a substance is isotonic with a 1.5 % solution of urea (molar mass =  $60\text{ g mol}^{-1}$ ) in the same solvent. If the densities of both the solutions are assumed to be equal to  $1.0\text{ g cm}^{-3}$ , molar mass of the substance will be  
 (a)  $115.0\text{ g mol}^{-1}$   
 (b)  $105.0\text{ g mol}^{-1}$   
 (c)  $210.0\text{ g mol}^{-1}$   
 (d)  $90.0\text{ g mol}^{-1}$
73. At  $80^\circ\text{C}$ , the vapour pressure of pure liquid 'A' is 520 mm Hg and that of pure liquid 'B' is 1000 mm Hg. If a mixture solution of 'A' and 'B' boils at  $80^\circ\text{C}$  and 1 atm pressure, the amount of 'A' in the mixture is (1 atm = 760 mm Hg).  
 (a) 52 mol per cent  
 (b) 34 mol per cent  
 (c) 48 mol per cent  
 (d) 50 mol per cent
74. Vapour pressure of pure A = 100 torr, moles = 2 vapour pressure of pure B = 80 torr, moles = 3 Total vapour pressure of mixture is  
 a. 187 torr  
 b. 450 torr  
 c. 44 torr  
 d. 88 torr
75. The vapour pressure of water at  $20^\circ\text{C}$  is 17.5 mm Hg. If 18 g of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) is added to 178.2 g of water at  $20^\circ\text{C}$ , the vapour pressure of the resulting solution will be  
 (a) 17.675 mm Hg  
 (b) 15.750 mm Hg  
 (c) 16.500 mm Hg  
 (d) 17.325 mm Hg.
- ### Brainteasers Objective Type Questions (Single choice only)
76. Solution  $S_1$  contains 6 g of urea per litre and solution  $S_2$  contains 18 g glucose per litre. At  $298\text{ K}$ , the osmotic pressure of  
 a.  $S_1 < S_2$   
 b.  $S_1 > S_2$   
 c. both the solution is 1 atm  
 d. both the solution is same
77. A 0.2 molal aqueous solution of a weak acid (HX) is 20% ionized. The freezing point of this solution is (Given  $K_f = 1.860\text{ C kg mol}^{-1}$  for water)  
 a.  $-0.45^\circ\text{C}$       b.  $-0.90^\circ\text{C}$   
 c.  $-0.21^\circ\text{C}$       d.  $-0.43^\circ\text{C}$
78. An aqueous solution of sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , containing 34.2 g/lit has an osmotic pressure of 2.38 atmospheres at  $17^\circ\text{C}$  for an aqueous solution of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$  to be isotonic with this solution, it would have

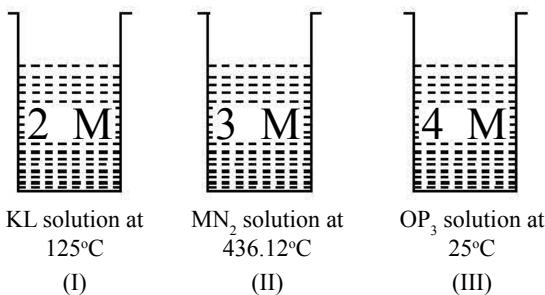
## 9.30 ■ Solutions and Colligative Properties

- a.** 18.0 g/lit      **b.** 16.2 g/lit  
**c.** 36.6 g/lit of glucose      **d.** 14.0 g/lit
- 79.** The freezing point of water is depressed by  $0.37^{\circ}\text{C}$  in a 0.01 molar NaCl solution. The freezing point of 0.02 molal solution of urea is dependent by  
**a.**  $0.37^{\circ}\text{C}$       **b.**  $0^{\circ}\text{C}$   
**c.**  $0.56^{\circ}\text{C}$       **d.**  $0.187^{\circ}\text{C}$
- 80.** The relative lowering of vapour pressure of an aqueous solution containing non-volatile solute is 0.0125. The molarity of the solution is  
**a.** 0.70      **b.** 0.45  
**c.** 0.34      **d.** 0.50
- 81.**  $\text{FeCl}_3$  reacts with  $\text{K}_4\text{Fe}(\text{CN})_6$  in aqueous solution to give blue colour if these two are separated by a s.p.m. as shown in the figure then due to osmosis
- Side A    S.P.M.    Side B
- a.** blue colour is formed towards side A  
**b.** blue colour is formed towards side B  
**c.** blue colour is formed on both the sides side  
**d.** no blue colouration
- 82.** The osmotic pressure of 0.1 M solution of  $\text{NaNO}_3$  and  $\text{CH}_3\text{COOH}$  are  $P_1$  and  $P_2$  respectively. thus,  
**a.**  $P_1 > P_2$       **b.**  $P_1 < P_2$   
**c.**  $P_1 = P_2$       **d.** 
$$\frac{P}{P_1 + P_2} = \frac{P}{P_1 + P_2}$$
- 83.** Two liquids X and Y form an ideal solution. The mixture has a vapour pressure of 400 mm at 300 K when mixed in the molar ratio of 1 : 1 and a vapour pressure of 350 mm when mixed in the molar ratio of 1 : 2 at the same temperature. The vapour pressures of the two pure liquids X and Y respectively are  
**a.** 250 mm, 590 mm  
**b.** 340 mm, 440 mm  
**c.** 230 mm, 210 mm  
**d.** 550 mm, 250 mm
- 84.** The osmotic pressure of a solution containing 4.0 g of solute (molar mass 246) per litre at  $27^{\circ}\text{C}$  is ( $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$ ).  
**a.** 0.1 atm      **b.** 0.3 atm  
**c.** 0.4 atm      **d.** 0.9 atm
- 85.** The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to  
**a.** ionization of benzoic acid  
**b.** dimerization of benzoic acid  
**c.** trimerization of benzoic acid  
**d.** solvation of benzoic acid
- 86.** A solution is prepared by dissolving 17.75 g  $\text{H}_2\text{SO}_4$ , in enough water to make 100.0 ml of solution. If the density of the solution is 1.1094 g/ml, what is the mole fraction  $\text{H}_2\text{SO}_4$  in the solution?  
**a.** 1.338  
**b.** 0.148  
**c.** 3.38  
**d.** 0.0338
- 87.** At 328 K ethanol has a vapour pressure of 168 mm and the vapour pressure of methyl cyclohexane is 280 mm. A solution of the two, in which the mole fraction of ethanol is 0.68, has a total vapour pressure of 376 mm. This solution formed from its components with  
**a.** The absorption of heat  
**b.** The evolution of heat  
**c.** Neither absorption nor evolution of heat  
**d.** Nothing can be said
- 88.** The vapour pressure of a solution of 5 g of non electrolyte in 100 g of water at a particular temperature is  $2985 \text{ Nm}^{-2}$ . The vapour pressure of pure water at that temperature is  $3000 \text{ Nm}^{-2}$ . The molecular weight of the solute is  
**a.** 180      **b.** 90  
**c.** 270      **d.** 360
- 89.** Acetic acid has boiling point of  $118.3^{\circ}\text{C}$  and freezing point of  $16.60^{\circ}\text{C}$ ;  $K_f$  and  $K_b$  are 3.57 and 3.07 deg/mole. The ratio of enthalpy of vaporization to that of fusion is  
**a.** 21.2      **b.** 1.065  
**c.** 4.25      **d.** 2.12
- 90.** A 33% (by weight) aqueous solution of  $\text{NH}_3$  has a density of  $0.892 \text{ g cm}^{-3}$ . Its molality and molarity are respectively

- a.** 28.97, 17.31      **b.** 17.31, 28.97  
**c.** 57.84, 34.62      **d.** 34.62, 57.84
- 91.** The molal elevation constant of water is 0.51. The boiling point of 0.1 molal aqueous NaCl solution is nearly  
**a.** 100.05°C      **b.** 100.1°C  
**c.** 100.2°      **d.** 101.0°C
- 92.** The depression in f.p. of 0.01 m aqueous solution of urea, sodium chloride and sodium sulphate is in the ratio  
**a.** 1 : 1 : 1      **b.** 1 : 2 : 3  
**c.** 1 : 2 : 4      **d.** 2 : 2 : 3
- 93.** Osmotic pressure of a solution is 0.0821 atm at a temperature of 300 K. The concentration in mole/lit will be  
**a.** 0.33      **b.** 0.066  
**c.**  $0.3 \times 10^{-2}$       **d.** 3
- 94.** Consider this figure and select the correct statement:
- |                         |                                         |
|-------------------------|-----------------------------------------|
| 0.1M<br>KCM<br>Solution | 0.05 M<br>BaCl <sub>2</sub><br>Solution |
| S.P.M.                  |                                         |
- a.** BaCl<sub>2</sub> flows towards the KCl solution  
**b.** KCl flows towards the BaCl<sub>2</sub> solution  
**c.** there will be no movement of any solution  
**d.** first KCl flows towards BaCl<sub>2</sub>, then reverse process takes place
- 95.** Commercial cold packs often contain solid NH<sub>4</sub>NO<sub>3</sub> and a pouch of water. The temperature of the pack drops as the NH<sub>4</sub>NO<sub>3</sub> dissolves in water. Therefore, for the dissolving of NH<sub>4</sub>NO<sub>3</sub> in water,  
**a.**  $\Delta H_{\text{soln}}$  is positive and  $\Delta S_{\text{soln}}$  is positive.  
**b.**  $\Delta H_{\text{soln}}$  is positive and  $\Delta S_{\text{soln}}$  may be negative or positive  
**c.**  $\Delta H_{\text{soln}}$  is negative and  $\Delta S_{\text{soln}}$  may be negative or positive  
**d.**  $\Delta H_{\text{soln}}$  is negative and  $\Delta S_{\text{soln}}$  is positive
- 96.** The freezing point of equimolal aqueous solution will be highest for  
**a.** C<sub>6</sub>H<sub>5</sub>N+H<sub>3</sub>C<sup>l-</sup> (aniline hydrochloride)  
**b.** Ca(NO<sub>3</sub>)<sub>2</sub>  
**c.** La(NO<sub>3</sub>)<sub>3</sub>  
**d.** C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> (Glucose)
- 97.** A sugar syrup of weight 214.2 g contains 34.2 g of water. The molal concentration is  
**a.** 0.55      **b.** 5.5  
**c.** 55      **d.** 0.1
- 98.** 5 ml of 1 N HCl, 20 ml of N/2 H<sub>2</sub>SO<sub>4</sub> and 30 ml of N/3 HNO<sub>3</sub> are mixed together and the volume made to one litre. The normality of the resulting solution is  
**a.** N/40      **b.** N/25  
**c.** N/20      **d.** N/10
- 99.** The ionic strength of a solution containing 0.1 mole/kg of KCl and 0.2 mole/kg of CuSO<sub>4</sub> is  
**a.** 0.2      **b.** 0.3  
**c.** 0.6      **d.** 0.9
- 100.** In a solution of an organic solute (mol. wt. = 180) in CCl<sub>4</sub>, where the solute is dimerised. 50 g of the solute are present per litre of the solution. The osmotic pressure of the solution is 4.11 atm at 27°C (Assume R = 0.082 lit atm K<sup>-1</sup> mol<sup>-1</sup>). The degree of association of the solute in CCl<sub>4</sub> is  
**a.** 75.5 %      **b.** 70 %  
**c.** 60 %      **d.** 80 %
- 101.** In 100 g of naphthalene, 2.423 g of S was dissolved. Melting point of naphthalene = 80.1°C.  $\Delta T_f$  = 0.661°C. L<sub>f</sub> = 35.7 cal/g of naphthalene. Molecular formula of sulphur added is  
**a.** S<sub>4</sub>      **b.** S<sub>8</sub>  
**c.** S<sub>2</sub>      **d.** S<sub>6</sub>
- 102.** Mole fraction of solute in benzene is 0.2, then the molality of the solution is  
**a.** 2      **b.** 4  
**c.** 3.2      **d.** 3.8
- 103.** Which one of the following aqueous solutions will exhibit highest boiling point?  
**a.** 0.05 M glucose  
**b.** 0.01 M KNO<sub>3</sub>  
**c.** 0.015 M urea  
**d.** 0.01 M Na<sub>2</sub>SO<sub>4</sub>

## 9.32 ■ Solutions and Colligative Properties

- 104.** A 1.03% solution of glycerine is isotopic with 2 % solution of glucose. What will be the molecular mass of glycerin?
- 92.7
  - 98.0
  - 90.2
  - 96.4
- 105.** Out of 1 N  $\text{HNO}_3$  and 1 N  $\text{H}_2\text{SO}_4$  aqueous solutions, which has higher boiling point?
- $\text{HNO}_3$
  - $\text{H}_2\text{SO}_4$
  - both have same boiling point
  - cannot be predicted
- 106.** A 5 % solution (by mass) of cane sugar in water has freezing point of 271 K and freezing point of pure water is 273.15 K. The freezing point of a 5 % solution (by mass) of glucose in water is
- 271 K
  - 273.15 K
  - 269.07 K
  - 277.23 K
- 107.** Amount of urea ( $\text{NH}_2\text{CONH}_2$ ) to be dissolved in 1 kg of water so that the value of the  $K_f = 105 \Delta T_f$
- 0.57 g
  - 1.14 g
  - 05.7 g
  - 0.96 g
- 108.** The vapour pressure of two liquids 'P' and 'Q' are 80 and 60 torr respectively. The total vapour pressure of solution obtained by mixing 3 mole of P and 2 mol of Q would be
- 20 torr
  - 72 torr
  - 68 torr
  - 140 torr
- 109.** Consider the following three solutions for 3 strong electrolytes. KL,  $\text{MN}_2$ ,  $\text{OP}_3$ .



The osmotic pressure ratio of I, II and III is

- 4:3:1
- 1:3 : 4
- 1 : 4 : 3
- 1: 1: 1

- 110.** Consider the following pairs of completely miscible liquids in order: water-dioxan, acetone-chloroform and ethylene dibromide-propylene dibromide. These will respectively show the following types of deviations from Raoult's law (in the vapour pressure curves)
- negative, positive, zero
  - positive, zero, negative
  - positive, negative, zero
  - zero, positive, negative
- 111.** The latent heat of vaporization of water is 9800 cal/mole and if the b.p. is 100°C, the ebullioscopic constant of water is
- 0.511°
  - 1.2 2°
  - 51.18°
  - 10.26°
- 112.** The osmotic pressure of urea solution is 500 mm at 10°C. If the solution is diluted and temperature is raised to 25°C, the osmotic pressure decreases to 105.3 mm, what is the extent of dilution?
- 2.5 times
  - 3.25 times
  - 5 times
  - 7.5 times
- 113.** 25 g of a binary electrolyte (molecular weight = 100) are dissolved in 600 g of water. The freezing point of the solution is  $-0.74^\circ\text{C}$ ;  $K_f = 1.86$  molarity-1. The degree of dissociation of the electrolyte is
- 0
  - 25 %
  - 66.5 %
  - 87.5 %
- 114.** Solution A contains 7 g/L  $\text{MgCl}_2$  and solution B contains 7 g/L of NaCl. At room temperature, the osmotic pressure of
- Both have same osmotic pressure
  - Solution B is greater than A
  - Solution A is greater than B
  - Cannot determined
- 115.** If two substances A and B have  $P^\circ\text{A} : P^\circ\text{B} = 1 : 2$  and have mole fraction in solution 1 : 2, then mole fraction of A in vapours is
- 0.2
  - 0.52
  - 0.25
  - 0.36
- 116.** Dry air is passed through a solution containing 10 g of the solute in 90 g of water and then through pure water. The loss in weight of solution is 2.5 g and that of pure solvent is 0.05 g. Calculate the molecular weight of the solute.

- a. 25  
c. 50

- b. 51  
d. 102

117. A 0.001 molal solution of a complex  $[MX_8]$  in water has the freezing point of  $-0.0054^\circ\text{C}$ . Assuming 100% ionization of the complex salt and  $K_f$  for  $\text{H}_2\text{O} = 1.86 \text{ Km}^{-1}$ , write the correct representation for the complex.

- a.  $[\text{MX}_6]\text{X}_2$   
b.  $[\text{MX}_5]\text{X}_3$   
c.  $[\text{MX}_8]$   
d.  $[\text{MX}_7]\text{X}$

118. A solution containing 0.1 g of a non-volatile organic substance P (molecular weight = 100) in 100 g of benzene raises the boiling point of benzene by  $0.2^\circ\text{C}$ , while a solution containing 0.1 g of another non-volatile substance Q in the same amount of benzene raises the boiling point of benzene by  $0.4^\circ\text{C}$ . What is the ratio of molecular weights of P and Q?

- a. 1 : 4  
b. 4 : 1  
c. 1 : 2  
d. 2 : 1

119. If the vapour pressures of pure A and pure B at 298 K are 60 and 15 torr respectively, what would be the mole percent of A in vapour phase (at this temperature) in a solution that contains 20 mole per cent of A in the (A + B) binary mixture in the liquid phase?

- a. 0.5  
b. 0.3  
c. 0.7  
d. 0.8

120. Concentrated aqueous sulphuric acid is 98%  $\text{H}_2\text{SO}_4$  by mass and has a density of  $1.80 \text{ g mL}^{-1}$ . Volume of acid required to make one litre of 0.1 M  $\text{H}_2\text{SO}_4$  solution is:

- a. 11.10 mL  
b. 16.65 mL  
c. 22.20 mL  
d. 5.55 mL

121. A decimolar solution of pot. ferrocyanide is 50 % dissociated at 300 K. calculate the osmotic pressure of the solution ( $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ )

- a. 0.74 atm  
b. 7.4 atm  
c. 76.89 atm  
d. 3.2

122. Which of the following plots represents the behaviour of an ideal binary liquid solution?

- a. Plot of  $P_{\text{total}}$  vs  $N_B$  is linear  
b. Plot of  $P_{\text{total}}$  vs  $N_A$  (mol fraction of A in vapour phase) is linear  
c. Plot of  $1/P_{\text{total}}$  vs  $N_B$  is non-linear  
d. Plot of  $1/P_{\text{total}}$  vs  $N_A$  is linear

123. pH of 0.1 M monobasic acid solution is found to be 2. Thus its osmotic pressure at T K is

- a. 0.011 ST  
c. 0.0011 ST

- b. 0.11 ST  
d. 1.11 ST

124. The number of millimoles of sodium chloride and magnesium chloride required to coagulate a litre each of two sols X and Y are as follows:

	X	Y
NaCl	51	46
MgCl <sub>2</sub>	71	23

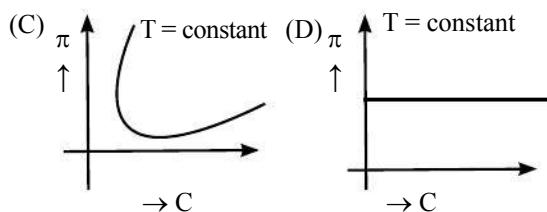
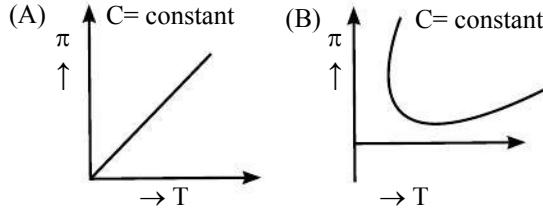
Which of the following would not be reasonable value to expect for the amount of the other salt required to cause precipitation?

- a. Y will be precipitated by 0.8 millimoles of  $\text{MgSO}_4$   
b. X will be precipitated by 25 millimoles of  $\text{Na}_2\text{SO}_4$   
c. Y will be precipitated by 0.3 millimoles of  $\text{AlCl}_3$   
d. X will be precipitated by 0.06 milli-moles of  $\text{AlCl}_3$

125. Van't Hoff proved that osmotic pressure ( $\pi$ ) is a colligative property and for an ideal solution, osmotic pressure ( $\pi$ ) is helpful to find that molecular mass of solute by using the relation

$$M_B = \frac{W_B R_T}{\pi \cdot V}$$

The law can be shown by which of these curve (C = concentration)?



**Multiple Correct Answer Type Questions**

- 126.** Which are the incorrectly matched statements?
- Water + HI – Minimum boiling point azeotrope
  - $\text{HNO}_3$  + Water – Endothermic solution
  - $\text{CHCl}_3$  +  $\text{CCl}_4$  – Endothermic solution
  - Acetic acid + pyridine – Hot solution
- 127.** The osmotic pressure of 0.1 M  $\text{Fe}_2(\text{SO}_4)_3$  aqueous solution is nearest to that of
- 0.1 M  $\text{CaCl}_2$
  - 0.1 M  $\text{Ca}_3[\text{PO}_4]_2$
  - 0.1 M  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
  - 0.1 M  $\text{K}_4[\text{Fe}(\text{CN})_6]$
- 128.** When two miscible liquids form an ideal solution, which of the thermodynamic properties is/are zero?
- $\Delta V$
  - $\Delta G$
  - $\Delta H$  only
  - $\Delta S$
- 129.** Increasing the temperature of an aqueous solution will not cause
- decrease in molality
  - decrease in molarity
  - decrease in mole fraction
  - decrease in % (w/w).
- 130.** Which of the following is/are colligative property?
- Osmotic pressure
  - Vapour pressure of solution
  - Depression in freezing point
  - Elevation in boiling point
- 131.** Which of the following is/are not correctly matched?
- |               |                        |
|---------------|------------------------|
| Solvent       | Ebullioscopic constant |
| a. Chloroform | 1.22                   |
| b. Water      | 1.86                   |
| c. Acetone    | 0.51                   |
| d. Benzene    | 2.53                   |
- 132.** Select the correct statements about the following solutions (assuming equal amount of each solute is dissolved in 1 lit solution)

1 lit  $\text{KCl}$ , 1 lit Urea, 1 lit  $\text{CaCl}_2$ , 1 lit  $\text{Mg}_3(\text{PO}_4)_2$ 

- a.** Boiling point:  
 $\text{KCl} > \text{urea} > \text{Mg}_3(\text{PO}_4)_2 > \text{CaCl}_2$
- b.** Freezing point:  
 $\text{Urea} < \text{KCl} < \text{Mg}_3(\text{PO}_4)_2 < \text{CaCl}_2$
- c.** Osmotic pressure:  
 $\text{KCl} > \text{urea} > \text{Mg}_3(\text{PO}_4)_2 > \text{CaCl}_2$
- d.** Freezing point:  
 $\text{KCl} > \text{urea} > \text{Mg}_3(\text{PO}_4)_2 > \text{CaCl}_2$
- 133.** Which is/are not true about ideal solutions?
- The entropy of mixing is zero
  - The enthalpy of mixing is negative
  - The volume of mixing is zero
  - The enthalpy of mixing is zero
- 134.** Dimmer of benzoic acid in benzene is in equilibrium with benzoic acid at a particular condition of temperature and pressure. If half of the dimmer molecules are hypothetically separated out then
- Freezing point of the solution reduces
  - Vapour pressure of the solution reduces
  - Osmotic pressure of the solution reduces
  - Boiling point of the solution reduces
- 135.** Which of the following liquid pairs show a negative deviation from Raoult's law?
- water – nitric acid
  - water – hydrochloric acid
  - benzene – methanol
  - acetone – chloroform
- 136.** Which one of the following statements is/are true?
- two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression
  - the osmotic pressure ( $\pi$ ) of a solution is given by the equation  $\pi = MRT$ , where M is the molarity of the solution
  - Raoult's law states that the vapour pressure of a component over a solution is proportional to its mole fraction
  - the correct order of osmotic pressure for 0.01 M aqueous solution of each compound is  $\text{BaCl}_2 > \text{KCl} < \text{CH}_3\text{COOH} > \text{Sucrose}$
- 137.** Consider the following arrangement and select the incorrect options .

0.2 M $\text{Na}_2\text{SO}_4$	0.18 M $\text{KCl}$
-----------------------------------	------------------------

Semipermeable membrane

- a. O.P. of  $\text{Na}_2\text{SO}_4$  solution is higher than the O.P. of KCl solution
- b. Water will flow from KCl solution to  $\text{Na}_2\text{SO}_4$  solution
- c. O.P. of  $\text{Na}_2\text{SO}_4$  solution is lesser than the O.P. of KCl solution
- d. Water will flow from  $\text{Na}_2\text{SO}_4$  solution to KCl solution
138. Which of the following statement is/are correct?
- a. Maximum boiling azeotropic mixture boils at temperature higher than either of the two pure components
- b. Minimum boiling azeotropic mixture boils at temperature lower than either of the two pure components
- c. Maximum boiling azeotropic mixture shows negative deviation
- d. Minimum boiling azeotropic mixture shows no deviation
139. To 22 ml 1 M  $\text{BaCl}_2$  solution 1<sub>2</sub> ml of 0.6 M  $\text{K}_2\text{SO}_4$  is added,  $\text{BaSO}_4$  is precipitated out.
- a. Vapour pressure is decreased
- b. boiling point is increased
- c. freezing point is increased
- d. freezing point is decreased
140. Which one of the statements given below concerning properties of solutions, can not describe a Colligative effect?
- a. boiling point of pure water decreases by the addition of ethanol
- b. vapour pressure of pure water decreases by the addition of nitric acid
- c. vapour pressure of pure benzene decreases by the addition of naphthalene
- d. boiling point of pure benzene increases by the addition of toluene

141. Which of the following solutions are isotonic with one another?
- a. 0.15 M urea
- b. 0.05 M  $\text{CaCl}_2$
- c. 0.1 M  $\text{MgSO}_4$
- d. 0.15 M glucose
142. Which of the following can not form(s) ideal solution?
- a. Ethyl alcohol + water
- b. Ethyl bromide + ethyl iodide
- c. Benzene + Toluene
- d. Chloroform + benzene
143. Which of the following is/are application/s of colligative properties?
- a. Melting snow by application of salt
- b. Reduced boiling points of pure liquids at increased altitudes
- c. Adding silver to mercury to lower the vapour pressure of mercury
- d. Desalinating sea water by reverse osmosis
144. 0.5 mol of  $\text{H}_2\text{SO}_4$  will exactly neutralize
- a. 1 mol of ammonia
- b. 0.5 mol of  $\text{Mg}(\text{OH})_2$
- c. 2 mol of  $\text{Ca}(\text{OH})_2$
- d. 1mol of KOH
145. 'V' litre decinormal solution of KCl is prepared. Half of the solution is converted into centinormal and added it into left decinormal solution. Then
- a. Number of milli equivalents of KCl do not change
- b. Number of milli moles of KCl are reduced by 1/5.
- c. Normality of the final solution becomes 0.01 N.
- d. Molarity of the final solution becomes 0.018 M.
146. Freezing point lowering expression can be given as  $\Delta T_f = K_f m$  (molality)
- Which of these assumption can be considered for the validity of the above relation?
- a. The  $\Delta H_f$  (latent heat of fusion of solvent) is independent of temperature between the actual and normal freezing point

## 9.36 ■ Solutions and Colligative Properties

- b.  $\Delta T_f$  is not equal to  $3K_f$  for 3 mol L<sup>-1</sup> solution.
  - c. The solid phase consists of pure solvent when solution is allowed to cool.
  - d. The solution is dilute

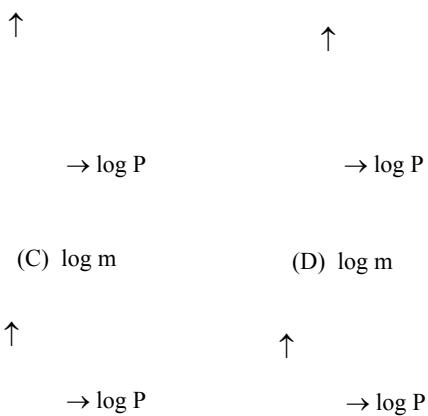
**147.** Consider following solutions:

- (I) 1M aqueous urea solution
  - (II) 1M aqueous potassium bromide solution
  - (III) 1M aqueous aluminium phosphate solution
  - (IV) 1M benzoic acid in benzene

Select correct statement(s) for the above solutions:

- a. III is hypertonic of I, II and IV.
  - b. II is hypotonic of III but hypertonic of I and IV.
  - c. IV is the hypotonic of I, II and III
  - d. All are isotonic solutions

**148.** Which of these curves do not represent Henry's law?



149. To 10 ml of 0.1 M  $\text{BaCl}_2$  solution 0.2 ml of 3 M  $\text{Na}_2\text{SO}_4$  is added. Assume  $\text{BaSO}_4$  formed on mixing is completely insoluble and the salts are completely dissociated as well as the change in volume is negligible. Point out the correct statement.

- a. Boiling point is increased
  - b. Freezing point is raised
  - c. Freezing point is lowered
  - d. Freezing point and boiling point do not change

150. A compound 'P' undergoes tetramerization in a given solvent 'Q'. Here correct statements are

- a. Observed freezing point  $\times 4$   
= Normal freezing point
  - b. Vant Hoff factor of compound is 0.25
  - c. Experimental boiling point  
= Calculated boiling point 4
  - d. Observed molar mass of solute  
 $= 4 \times$  Normal molar mass

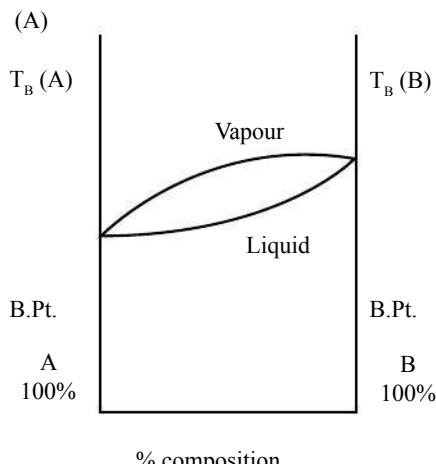
## **Linked-Comprehension Type Questions**

## Comprehension 1

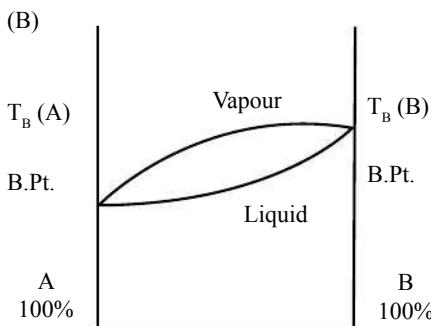
The vapour pressure of a solvent is lowered by the presence of the non – volatile solute in the solution and this lowering of vapour pressure of the solvent is governed by Raoult's law., according to which the relative lowering of vapour pressure of the solvent over a solution is equal to the mole fraction of a non- volatile solute present in the solution. However, in a case of binary liquid solution, if both the components of the solution are volatile then another form of Raoult's law is used. Mathematically, this form of the Raoult's law can be given as :

$P_{\text{total}} = P_1^0 x_1 + P_2^0 x_2$ . Solution which obey Raoult's law over the entire range of concentration are known as ideal solution. Two types of deviation from Raoult's law, that is, positive and negative deviations are observed. Azeotrops arise due to very large deviation from Raoult's law.

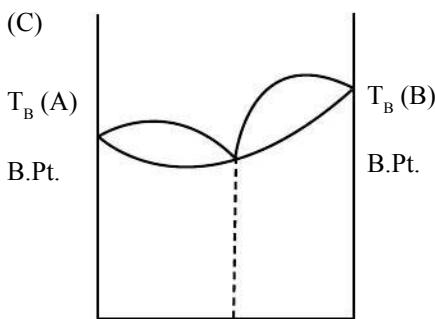
**151.** When a plot of boiling point versus composition is plotted, then the type of graph that cannot be obtained is



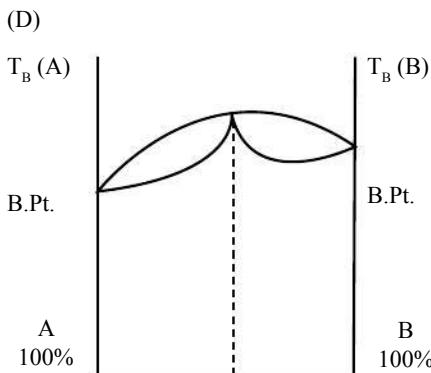
For ideal solution with  $P^o_A > P^o_B$



For ideal solutions with  $P_A^o < P_B^o$



For non-ideal solution with +ve deviation



For non-ideal solution with -ve deviation

- 152.** Select the correct option for an ideal solution:

- (i)  $\Delta H_{\text{mix}} = 0, \Delta V_{\text{mix}} = 0$
- (ii)  $\Delta S_{\text{mix}} > 0, \Delta V = 0$
- (iii)  $\Delta H_{\text{mix}} = 0, \Delta S > 0$
- (iv)  $V_{\text{Pobs.}} > V_{\text{Pexp.}}$

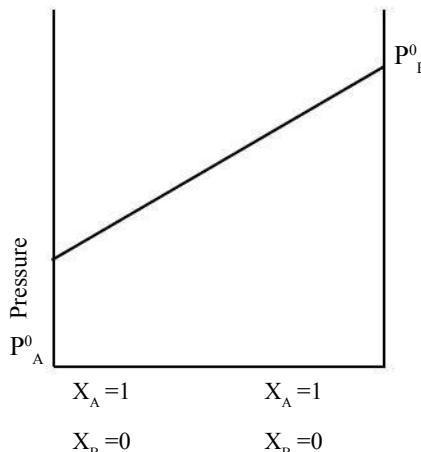
- a. (i), (ii), (iii), (iv)

- b. (i), (ii), (iii)

- c. (ii), (iii), (iv)

- d. (i), (ii)

- 153.** Consider the following graph plotted between the vapour pressure of two volatile liquids against their respectively mole fraction and select the correct options.



Mole fraction

- a. When  $x_A = 1$  and  $x_B = 0$ , then  $P = P_A^o$
- b. When  $x_B = 1$  and  $x_A = 0$ , then  $P = P_B^o$
- c.  $x_A = 0$  and  $x_B = 0$ , then  $P < P_B^o$
- d. Both A, B

## Comprehension 2

The actual values of colligative properties in most of the cases are equal to expected values. Whenever there is dissociation or association the values differ it means colligative properties become abnormal.

Van't Hoff introduced a new factor 'i' to explain the abnormal colligative properties.

- 154.** In case of dissociation, which of the following increases,

- (i) Vapour pressure
- (ii) Freezing Point
- (iii) Boiling point
- (iv) Osmotic pressure

- a. (i), (iii), (iv)

- b. (ii), (iii), (iv)

- c. (iii), (iv)

- d. (ii), (iii)

## 9.38 ■ Solutions and Colligative Properties

- 155.** Which of the following represents the decreasing order of  $\Delta T_b$ ?
- 0.02 M Glucose
  - 0.01 M  $KCl$
  - 0.02 M  $CaF_2$
  - 0.01 M  $AlCl_3$
- a.** (iv) > (iii) > (ii) = (i)  
**b.** (iii) > (iv) > (ii) = (i)  
**c.** (iii) > (iv) > (ii) > (i)  
**d.** (iv) > (iii) > (ii) > (i)
- 156.** Find the value of van't Hoff factor for 0.1 M  $Ca(NO_3)_2$  solution if degree of dissociation of 0.87 for it
- a.** 1.74                    **b.** 2.74  
**c.** 2.84                    **d.** 2.62
- 157.** If we take 1L solution at 300 K of 0.1 M sucrose, 0.05 M KCl, 0.1  $CaCl_2$  and 0.1  $AlCl_3$ . The correct ratio of osmotic pressure for these respectively can be given as:
- a.** 1 : 2 : 3 : 4  
**b.** 1 : 1 : 3 : 4  
**c.** 1 : 1 : 2 : 4  
**d.** 1 : 1 : 1 : 4
- 159.** The van't Hoff factor is
- $i = 1 + \alpha$
  - $i = 1 + \alpha/2$
  - $i = 1 - \alpha/2$
  - $i = 1 - 2\alpha$
- 160.** The degree of association can be given as
- $\alpha = \frac{\Delta T_b}{2K_{bx}}$
  - $\alpha = \frac{2 + 2\Delta T_b}{K_{bx}}$
  - $\alpha = \frac{2(K_{bx} - \Delta T_b)}{K_{bx}}$
  - $\alpha = \frac{(K_{bx} - \Delta T_b)}{\Delta T_b \cdot 2}$
- 161.** When 0.55 g of pure benzoic acid,  $C_7H_6O_2$ , is dissolved in 32.0 g of benzene, the freezing point of the solution is measured to be 0.36°C lower than the freezing point value of 5.50°C for the pure solvent. Calculate the molecular weight of benzoic acid in benzene.
- a.** 242.4                    **b.** 244.4  
**c.** 245.2                    **d.** 122.2

### Comprehension 3

A dilute solution having 'n' moles of a solute P in 1 kg of solvent with molal elevation constant  $K_b$ . It dimerises in the solution according to the equation given below

$$2P \rightleftharpoons P_2$$

The degree of association can be given as

$$\alpha_{assoc.} = \frac{i-1}{1/n-1}$$

- 158.** Which of the following is not true here incase of association?

- $\Delta T_{obs.} > \Delta T_{exp.}$
  - $O.P_{obs.} > O.exp.$
  - $\Delta T_{obs.} > \Delta T_f_{exp.}$
  - Mol. Wt<sub>obs.</sub> > Mol. Wt<sub>exp.</sub>
- (i), (ii)
  - (ii), (iii)
  - (i), (ii), (iii)
  - (ii), (iii), (iv)

### Comprehension 4

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution M is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9

Given :Freezing point depression constant of water ( $K_f$  water) = 1.86 K kg mol<sup>-1</sup>

Freezing point depression constant of ethanol ( $K_f$  ethanol) = 2.0 k kg mol<sup>-1</sup>

Boiling point elevation constant of water

( $K_b$  water) = 0.52K kg mol<sup>-1</sup>

Boiling point elevation constant of ethanol ( $K_b$  ethanol) n= 1. K kg mol<sup>-1</sup>

Standard freezing point of water = 273 K

Standard freezing point of ethanol = 155.7 K

Standard boiling point of water = 373 K

Standard boiling point of ethanol = 351.5 K

Standard pressure of pure water = 32.8 mm Hg

Standard pressure of pure ethanol = 40 mm Hg

Molecular weight of water = 18 g mol<sup>-1</sup>

Molecular weight of ethanol = 46 g mol<sup>-1</sup>

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

**162.** The freezing point of the solution M is

- a. 268.7 K
- b. 268.5 K
- c. 234.2 K
- d. 150.9 K

**163.** The vapour pressure of the solution M is

- a. 39.3 mm Hg
- b. 36.0 mm Hg
- c. 29.5 mm Hg
- d. 28.8 mm Hg

**164.** Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is

- a. 380.4 K
- b. 376.2 K
- c. 375.5 K
- d. 354.7 K

### Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given. Mark.

- a. if A and R both are correct and R is the correct explanation of A;
- b. if A and R both are correct but R is not the correct explanation of A;
- c. A is true but R is false;
- d. A is false but R is true;
- e. A and R both are false.

**165.** (A): Camphor is used as a solvent in the determination of molecular weight of non-volatile solute.

(R): Camphor has high molal elevation constant.

**166.** (A): When a cell is placed in hypertonic solution, it shrinks

(R): Reverse osmosis is used for desalination of water.

**167.** (A): When  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is dissolved in water, the solution cools down and when  $\text{CuSO}_4$  is dissolved in water, the solution gets heated up.

(R): The dissolution of hydrated  $\text{CuSO}_4$  is endothermic process because force of attraction decreases on dissolution whereas  $\text{CuSO}_4$  (anhydrous) changes to hydrated and energy is released due to formation of new bonds.

**168.** (A): Addition of ethylene glycol to water lowers the freezing point of water, therefore, used as anti-freeze.

(R): 1, 2-Ethanediol is soluble in water because it can form H-bond with water, therefore vapour pressure of solution is lowered.

**169.** (A): All solutes become more soluble in water at higher temperature

(R): The amount of solute that dissolve depends upon the mature temperature and pressure (gases) of the substance

**170.** (A): The vapour pressure of 0.45 molar urea solution is more than that of 0.45 molar solution of sugar.

(R): Lowering of vapour pressure is directly proportional to the number of species present in the solution.

**171.** (A): An increase in surface area increases the rate of evaporation

(R): Stronger the inter-molecular attraction forces, faster in the rate of evaporation at a given temperature

**172.** (A): The freezing point of 0.1 M urea is less than that of 0.1 M KCl solution

(R): The depression of freezing point is directly proportional to the number of species present in the solution.

**173.** (A): The freezing point of 0.05 M urea solution is different from that of 0.05 M sodium chloride solution.

(R): The depression in freezing point is directly proportional to the number of species present in the solution.

**174.** (A): The vapour pressure of 0.1 M sugar solution is more than that of 0.1 M potassium chloride solution.

(R): Lowering of vapour pressure is directly proportional to the number of species present in the solution.

**175.** (A): Acetic acid has molecular weight of 120 in benzene solution.

(R): There is dimer formation by H-bonding.

## 9.40 ■ Solutions and Colligative Properties

176. (A): The boiling point of 0.1 urea solution is less than that if 0.1 M KCl solution.
- (R): Elevation of boiling point is directly proportional to the number of species present in the solution
177. (A): If one component obeyed Raoult's law over a certain range of composition, the other component would not obey Henry's law in that range.
- (R): Raoult's law is a special case of Henry's law.
178. (A): Strength and Normality are two different methods of expressing the concentration of a solution.
- (R): Strength is equal to normality of a solution.
179. (A): One molar aqueous solution has always higher concentration than one molal.
- (R): The molality of a solution depends upon the density of the solution whereas molarity does not.
180. (A): Osmosis involves movement of solvent molecules from its lower concentration to its higher concentration.
- (R): Solution having the same osmotic pressure are called isotonic solution.
181. (A): The vapour pressure of a liquid decreases if some non-volatile solute is dissolved in it.
- (R): The relative lowering of vapour pressure of a solution containing a non volatile solute is equal to the mole fraction of the solute in the solution.
182. (A): Solutions show deviations from Raoult's law.
- (R): The cause for these deviations lies in the nature of interactions at the molecular level.
183. (A): Vapour pressure of water is less than 1.013 bar at 373 K.
- (R): Water boils at 373 K as the vapour pressure at this temperature becomes equal to atmospheric pressure .
184. (A): A Azeotropic liquid mixture is one that boils with unchanged composition.
- (R): The vapour pressure of a liquid decreases upon dissolution of a non volatile liquid which is attributable to its some kind of association with non-volatile solute.
185. (A): Introduction of Van't Hoff factor signifies the change in molalities with respect to number of particles present in solution after dissociation or association.
- (R): Van't Hoff factor can be neglected if molality remains the same.
186. (A): Molecular mass of polymers cannot be calculated using boiling point or freezing point method.
- (R): Polymers solution do not possess a constant boiling point or freezing point.
187. (A): One molal aqueous solution of urea contains 60 g of urea in 1000 g water.
- (R): Solution having one mole of solute in 1000 g solvent is called as one molal solution.
188. (A): Elevation in boiling point will be high if the molal elevation constant of the liquid is high.
- (R): Elevation in boiling point is a colligative property.
189. (A): Azeotropic mixture are formed only by non-ideal solutions.
- (R): Boiling point of an azeotropic is either higher than both the components or lower than both the components.
190. (A): The mobility of sodium ions is lower than that of potassium ion.
- (R): The ionic mobilities depend upon the effective radius of the ion.
191. (A): When dried fruits and vegetables are placed in water, they slowly get swelled.
- (R): It happens due to the phenomenon of osmosis.

### Matrix-Match Type Questions

192. Match the following:

Column I	Column II
A. Osmotic pressure	(p) Colligative Property
B. Relative lowering of V.P.	(q) Ostwald Walker Method
C. Elevation in B.P.	(r) $\alpha / \text{molecular weight of solute}$
D. Depression in F.P.	(s) Ebullioscopic constant
	(t) Cryoscopic constant

**193.** Match the following for an ideal solution:

<b>Column I</b>	<b>Column II</b>
A. $\Delta H$	(p) observed vapour pressure
B. $\Delta V$	(q) equals to A–A or B–B
C. A–B interaction	(r) zero
D. total vapour pressure	(s) positive

**194.** Match the following:

<b>Column I (Solute)</b>	<b>Column II (Van't Hoff factor, i)</b>
A. $\text{FeCl}_3$ if $\alpha = 0.8$	(p) $i = 3.4$
B. $\text{CaCl}_2$ if $\alpha = 0.9$	(q) $i = 2.8$
C. $\text{K}_3\text{PO}_4$ if $\alpha = 0.9$	(r) $i = 3.8$
D. $\text{Al}_2(\text{SO}_4)_3$ if $\alpha = 0.7$	(s) $i = 3.7$

**195.** Match the following

<b>Column I</b>	<b>Column II</b>
A. Normality	(p) gram of solute in one lit.
B. Molarity	(q) no. of mole in one kg solvent
C. Molality	(r) no. of mole in one lit.
D. Concentration	(s) no. of w/E in one lit

**196.** Match the following:

<b>Column I</b>	<b>Column II (Here <math>\alpha</math> = degree of ionization)</b>
A. $\text{K}_4[\text{Fe}(\text{CN})_6]$	(p) 1
B. $\text{Fe}_2(\text{SO}_4)_3$	(q) $1 + \alpha$
C. $\text{NH}_2 - \text{CO} - \text{NH}_2$	(q) $1 + \alpha$
D. $\text{BaCl}_2$	(r) $1 + 4\alpha$
	(s) Greater than 1

**197.** Match the following:

<b>Column I</b>	<b>Column II</b>
A. Benzene + Toluene	(p) Ideal Solution
B. Acetone + Chloroform	(q) Can be separated by fractional distillation

C. Ethyl Chloride + Ethyl Bromide (r) Can not be separated by fractional distillation completely

D. Ethyl Alcohol + Water (s) Maximum boiling Azetope.  
(t) Minimum boiling Azetope.

**198.** Match the value of molarity with normality here.

<b>Column I</b>	<b>Column II</b>
A. 0.02 M HCl	(p) 0.01 N HCl
B. 0.01 M HCl	(q) 0.02 N HCl
C. 0.001 M $\text{Ca}(\text{OH})_2$	(r) 0.006 N $\text{Al}(\text{OH})_3$
D. 0.002 M $\text{Al}(\text{OH})_3$	(s) 0.002 N $\text{Ca}(\text{OH})_2$

**199.** Match the following:

<b>Column I</b>	<b>Column II</b>
A. Molality	(p) $\frac{\% \text{mass} \times d \times 10}{M_B}$
B. Mole fraction of solute	(q) $\frac{\% \text{mass} \times d \times 10}{E_B}$
C. Normality	(r) $\frac{M \times 10^3}{1000d - MM_B}$
D. Molarity	(s) $\frac{mM_A}{1 + mM_A}$

**200.** Match the following:

<b>Column I</b>	<b>Column II</b>
A. 0.1 M $\text{Fe}_2(\text{SO}_4)_3$	(p) Solution with highest boiling point
B. 0.1 M $\text{AlPO}_4$	(q) Van't Hoff factor is greater than 1
C. 0.1 M Glucose	(r) Solution with lowest osmotic pressure
D. 0.1 M $\text{CaCl}_2$	(s) Solution with lowest freezing point

The IIT-JEE Corner

- 201.** The van't Hoff factor for 0.1 M  $\text{Ba}(\text{NO}_3)_2$  solution is 2.74. The degree of dissociation is

  - a. 91.4 %
  - b. 87 %
  - c. 100 %
  - d. 75 %

[IIT 1999]



[HT 1999]

- 203.** To  $500 \text{ cm}^3$  of water,  $3.0 \times 10^{-3} \text{ kg}$  of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point?  $K_f$  and density of water at  $1.86 \text{ K kg}^{-1}$  and  $0.0997 \text{ g cm}^{-3}$  respectively.

a. 0.186 K      b. 0.228 K  
c. 0.371 K      d. 0.555 K

[HT 2000]

- 204.** An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 ml. The volume of 0.1 N NaOH required to completely neutralize 10 ml of this solution is

a. 40 ml                          b. 20 ml  
c. 10 ml                           d. 4 ml

[ITF2001]

- 205.** During depression of freezing point in a solution which of the following are in equilibrium?

- a. liquid solvent, solid solvent
  - b. liquid solvent, solid solute
  - c. liquid solute, solid solute
  - d. liquid solute, solid solvent

[IIT 2003]

- 206.** A 0.004 M solution of  $\text{Na}_2\text{SO}_4$  is isotonic with a 0.010 M solution of glucose at same temperature. The apparent degree of dissociation of  $\text{Na}_2\text{SO}_4$  is

- a. 25%                          b. 50%  
c. 75%                          d. 85%

[HT 2004]

- 207.** The elevation in boiling point for 13.44 g of  $\text{CuCl}_2$  dissolved in 1 kg of water as solvent will be

( $K_b = 0.52 \text{ kg/J}$ , molar mass of  $\text{CuCl}_2 = 134.4 \text{ g/mol}$ )

- a.** 0.05      **b.** 0.10  
**c.** 0.16      **d.** 0.20

[IIT 2005]

- 208.** When 20 g of naphthoic acid ( $C_{11}H_8O_2$ ) is dissolved in 50 g of benzene ( $K_f = 1.72 \text{ K g mol}^{-1}$ ), a freezing point depression of 2 K is observed. The Van't Hoff factor ( $i$ ) is



[IIT 2007]

- 209.** The Henry's law constant for the solubility of  $N_2$  gas in water at 298 K is  $1.0 \times 10^5$  atm. The mole fraction of  $N_2$  in air is 0.8. The number of moles of  $N_2$  from air dissolved in 10 moles of water at 298 K and 5 atm pressure is

- a.**  $4.0 \times 10^{-4}$       **b.**  $4.0 \times 10^{-5}$   
**c.**  $5.0 \times 10^{-4}$       **d.**  $4.0 \times 10^{-6}$

[IIT 2009]

## ANSWERS

## Straight Objective Type Questions

**Brainteasers Objective Type Questions**

76. a    77. a    78. a    79. a    80. a    81. d    82. a    83. d    84. c    85. d    86. d    87. a  
 88. a    89. d    90. a    91. a    92. b    93. c    94. c    95. a    96. d    97. a    98. a    99. d  
 100. d    101. b    102. c    103. c    104. a    105. a    106. c    107. a    108. b    109. c    110. c    111. a  
 112. c    113. a    114. b    115. a    116. d    117. a    118. d    119. a    120. d    121. b    122. d    123. b  
 124. c    125. a

**Multiple Correct Answer Type Questions**

126. a, b    127. b, d    128. a,c,d    129. a,c,d    130. a,c,d    131. a,b,c    132. a,c  
 133. a,b    134. c,d    135. a,b,d    136. b,c,d    137. c,d    138. a,b,c    139. a,b,d  
 140. a,b,d    141. a,b,d    142. a,d    143. a,c,d    144. a,b,d    145. a,d    146. a,b,d  
 147. a,b,c    148. b,c,d    149. a,c    150. b,c,d

**Linked-Comprehension Type Questions****Comprehension 1**

151. b    152. b    153. d

**Comprehension 2**

154. c    155. b    156. b    157. b

**Comprehension 3**

158. c    159. c    160. c    161. b

**Comprehension 4**

162. d    163. b    164. b

181. b    182. a    183. d    184. b  
 185. b    186. c    187. a    188. b  
 189. b    190. a    191. a

**Matrix-Match Type Questions**

192. a – (p, r), b – (p, q, r), c – (p, r, s), d – (p, r t)  
 193. a – (r), b – (r), c – (q) , d – (p)  
 194. a – (p), b – (q), c –(s), d (r)  
 195. a – (s), b – (r), c –(q), d – (p)  
 196. a –(r, s), b –(r, s), c –(p), d –(q, s)  
 197. a – (p, q), b – (r, s), c – (p, q), d – (r, t)  
 198. a – (q), b – (p), c – (s), d – (r)  
 199. a – (r), b – (s) , c – (q), d – (p)  
 200. a – (p, q, s) , b – (q), c – (r), d – (q)

**Assertion-Reason Type Questions**

165. a    166. b    167. a    168. a  
 169. b    170. d    171. c    172. d  
 173. a    174. a    175. a    176. c  
 177. d    178. c    179. b    180. b

**The IIT-JEE Corner**

201. b    202. c    203. b    204. a    205. a    206. c    207. c    208. b    209. a

## Hints and Explanations

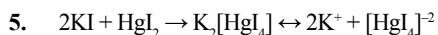
### Straight Objective Type Questions

2. As temperature of the two phases is same, their average K.E. is same.

3. 1 molal solution is the one which contains one mole of a solute in 1000 g of the solvent

4.  $\pi = CRT$

$$C = \frac{\pi}{RT} = \frac{0.0821}{0.0821 \times 300} \\ = 0.3 \times 10^{-2} \text{ mol L}^{-1}$$



there is a decrease in the number of ions present in the solution so  $\Delta T_f$  decrease or f.p. is raised.

6. Wt. of sugar solution = 214.2 g

Wt. of sugar = 34.2 g

Wt. of water =  $214.2 - 34.2 = 180 \text{ g}$

Molality =  $W_2/M_2 \times 1000 \times W_1$

$$= 34.2/342 \times 1000/180 = 0.55 \text{ m}$$

7. Number of ions formed

Urea : NaCl :  $\text{Na}_2\text{SO}_4$

0.01 mole :  $0.01 \times 2$  mole :  $0.01 \times 3$  mole

1 : 2 : 3

Thus  $\Delta T_f$  is also in the same ratio

( $\Delta T_f \propto i$  when molality is constant)

8. Except glucose, all other are electrolytes undergoing dissociation ( $i > 1$ ). Glucose is non electrolyte,  $i = 1$ . so it has least value of  $\Delta T_f$  and f.p. is maximum.

9.  $\Delta T_b = K_b \cdot m = 0.51 \times 0.1 = 0.051^\circ\text{C}$

now b.p. of solution =  $100 + \Delta T_b$

$$= 100 + 0.051$$

$$= 100.051^\circ\text{C}$$

12. When a non-volatile solute is added to the solvent, f.p. of solution gets depressed so it is the solvent (water) which first separates as ice on freezing.



Moles of  $\text{Fe}^{2+}$  formed

$$= \frac{1}{2} \times \text{moles of HCl used} \\ = \frac{1}{2} \times \frac{0.4 \times 500}{1000} = 0.1$$

14.  $\frac{p^o - ps}{p} = \frac{W_2}{M_2} \times \frac{M_1}{W_1}$

$$\frac{M_2 = W_2 \cdot M_1}{(p^o - ps/p^o) \cdot W_1}$$

$$= \frac{5 \times 18}{(3000 - 2985/3000) \times 100}.$$

On solving,

$$M_2 = 180.$$

15. Osmotic pressure

$$P = h \rho g$$

$$= (2.4 \times 10^{-3} \text{ m}) (0.88 \times 10^3 \text{ kgm}^{-3})$$

$$= 20.7 \text{ Pa} = 2.7 \text{ Nt./m}^2$$

$$\text{molarity} = P/RT$$

$$= \frac{20.7 \text{ Nt./m}^2}{8.314 \text{ J/kmol} \times 298 \text{ K}}.$$

$$M = 8.3 \times 10^{-3} \text{ mol/m}^3$$

$$= 8.3 \times 10^{-3} \text{ mol/L.}$$

16. At constant volume and pressure

$$T_1/T_2 = W_1 m_2/W_2 m_1$$

After putting the values and solving

$$T_2 = 100.25^\circ\text{C.}$$

17. Molarity decreases, volume increases with increase in temperature.

19. Benzoic acid exists as a dimer because of hydrogen bonding.

20.  $\pi = \frac{W_2 \cdot RT}{M_2} \cdot V = \frac{4 \times 0.082 \times 300}{246 \times 1}$

$$\pi = 0.4 \text{ atm}$$

21.  $\frac{P^o - P_s}{P^o} = x_2$

$$x_2 = \frac{0.80 - 0.60}{0.80} = 0.25$$

22. Addition of a non-volatile solute to water increases its boiling point. Thus, egg will be boiled earlier.

24. Solvent = Chloroform ( $K_b = 3.63^\circ$ )

Benzene ( $K_b = 2.53^\circ$ )

Acetone ( $K_b = 1.72^\circ$ )

Ethyl alcohol ( $K_b = 1.20^\circ$ )

25. The ratio of molar concentrations of particles will be  $1 : 1 : 2$ .

26. The beans are cooked earlier in pressure cooker because boiling point increases with increasing pressure.

27. According to Van't Hoff

$$\pi V = nST$$

$$\pi V = \frac{w}{m} ST \quad \text{or} \quad m = \frac{wST}{\pi V}$$

Given,  $w = 20 \text{ g}$ ,  $S = 0.0821$

$$T = 15 + 273 = 288^\circ\text{C}$$

$$\pi = 600 \text{ mm} = 600/760 \text{ atm}$$

$$V = 500 \text{ ml} = 0.5 \text{ litre}$$

So

$$m = \frac{20 \times 0.0821 \times 288 \times 760}{600 \times 0.5} = 1198$$

29.  $1500 \text{ cm}^3$  of  $0.1 \text{ N HCl}$  contains  $\text{HCl} = \frac{0.1}{1000} \times 1500 = 0.15 \text{ g eq.}$

It will neutralize  $0.15 \text{ g eq. of NaOH}$

$$= 0.15 \times 40 = 6 \text{ g.}$$

30. As  $N_1 V_1 = N_2 V_2$

$$100 \times 0.5 = 0.1 \times V_2$$

On solving, we get

$$V_2 = 500 \text{ cm}^3$$

So volume of water to be added

$$= 500 - 100 = 400 \text{ cm}^3.$$

31.  $X_A = 2/5 = 0.4, X_B = 0.6$

$$P_A = X_A P_A^o$$

$$= 0.4 \times 120 = 48 \text{ mm}$$

$$P_B = X_B P_B^o$$

$$= 0.6 \times 180 = 108 \text{ mm}$$

So, total vapour pressure

$$= 48 + 108 = 156 \text{ mm.}$$

32.  $\frac{P^o - P_s}{P_s} = \frac{n_B}{n_A}$

$$\text{or } \frac{7}{93} = \frac{n_B}{1000/18}.$$

$$n_B = \frac{1000}{18} \times \frac{7}{93} \cong 4.18$$

33.  $0.01 \text{ M Na}_3\text{PO}_4$  give more number of ions hence more lowering in vapour pressure. Thus it has least vapour pressure.

34. As  $\text{Na}_3\text{PO}_4$  gives maximum particles that is, 4 on dissociation so lowering of vapour pressure will be maximum.

37.  $\Delta T_b = mK_b$

$$\Delta T_f = m K_f$$

$$\frac{\Delta T_b}{\Delta T_f} = \frac{K_b}{K_f} = \frac{0.512}{1.86}$$

$$\Delta T_b = \frac{0.512}{1.86} \times 0.186 = 0.0512^\circ$$

38. According to distribution law, the ratio of the concentrations of the solute in the two immiscible liquids in constant at constant temperature.

39.  $\Delta T_f = \text{molality} \times K_f x_i$

$$= 0.2 \times 1.85 \times 1.3$$

$$= 0.481^\circ$$

$$\text{FP} = -0.481^\circ\text{C}$$

## 9.46 ■ Solutions and Colligative Properties

40. For ideal solution,

$$\Delta H_{\text{solution}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

41. Camphor is often used in molecular mass determination because of its high cryoscopic constant (37.7). This method is known as Rast's camphor method.

42.  $\frac{P^o - P_s}{P^o} = X_2$

$$\frac{760 - 750}{760} = X_2$$

$$X_2 = 10/760$$

$$= 1/76.$$

43. Total number of equivalents

$$= 2.5 \times 1 + 0.5 \times 3 = 4$$

$$\text{Molarity} = \frac{4}{3 + 2.5} = \frac{4}{5.5} = 0.73$$

44. The azeotropic mixture cannot be separated into individual components because both the components boil at the same temperature.

47. Assume X L of 4 N HCl are taken.

$$\text{Then } 10 \text{ N HCl taken} = (1 - X) \text{ L}$$

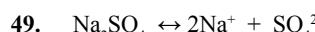
$$\text{According to, } N_1 V_1 + N_2 V_2 = N_3 V_3$$

$$4 \times X + 10(1 - X) = 6 \times 1$$

$$6X = 4$$

$$X = 4/6 = 0.67 \text{ L}$$

48. NaCl is an electrolyte which dissociates to give ions. Concentration of ions in the solution = 4 M. Glucose and urea are non electrolytes. As glucose has minimum concentration so it has minimum osmotic pressure.



1	0	0
1 - $\alpha$	$2\alpha$	$\alpha$

Vant Hoff Factor (i)

$$= \frac{1 - \alpha + 2\alpha + \alpha}{1} = 1 + 2\alpha.$$

50. Benzoic acid associates in benzene as



The number of particles decreases and hence osmotic pressure decreases.

53. Ionic percentage =  $\frac{\mu_{\text{calculated}}}{\mu_{\text{expected}}} \times 100$   
 $= \frac{1.03}{6.12} \times 100 = 17$

56. When system shows positive deviation from Raoult's law the vapour pressure increases where as boiling point decreases.

57. In the osmosis solvent passes through the membranes in which direction where concentration is high.

58. For isotonic solution

$$W_1/M_1 V_1 = W_2/M_2 V_2$$

$$\frac{10}{60 \times 1000} = \frac{5}{M_2 \times 100}.$$

on solving

$$M_2 = 300 \text{ gm/mole}$$

59.  $\frac{\Delta T = 1000 \times K_f \times w}{W \times m}$

$$\text{So } \Delta T = \frac{1000 \times 5.12 \times 1}{250 \times 51.2} = 0.4 \text{ K}$$

$$\frac{60. P^o - P_s}{P_s} = \frac{n}{N} = \frac{18 \times 18}{180 \times 178.2} = 0.01$$

$$(P^o = 760 \text{ torr})$$

$$\frac{760 - P_s}{P_s} = 0.01$$

61. Only  $\text{C}_6\text{H}_{12}\text{O}_6$  does not dissociate. As its number of particles in the solution is minimum so depression in freezing point is minimum or the actual freezing point is highest.

62. As  $\text{HNO}_3 + \text{H}_2\text{O}$  solution shows negative deviation from ideal behaviour so it forms azeotrope with maximum boiling point.

63. Lowering in freezing point is a colligative properties, colligative property depends on the number of molecule atom or ions and molality. In 0.1 m NaCl. Molality is maximum out of four and NaCl dissociate into  $\text{Na}^+$  +  $\text{Cl}^-$ .

64. 5 L dilute solution = 5000 ml = 5000 g  
 $= 5 \times 10^6 \text{ mg}$

ppm of  $\text{CaCO}_3$  in solution

$$= \frac{25}{5 \times 10^6} \times 10^6 = 5 \text{ ppm.}$$

65.  $X_A = 3/5 = 0.6$

$$X_B = 0.4$$

$$P_{\text{total}} = X_A P_A^\circ + X_B P_B^\circ$$

$$184 = 0.6 \times 200 + 0.4 \times P_B^\circ$$

$$0.4 P_B^\circ = 184 - 120 = 64$$

$$P_B^\circ = \frac{64}{0.4} = 160 \text{ torr.}$$

66.  $\text{HX} \rightleftharpoons \text{H}^+ + \text{X}^-$

$$1 - \alpha \quad \alpha \quad \alpha$$

$$\text{Total} = 1 + \alpha$$

$$\text{So } i = 1 + \alpha = 1 + 0.2 = 1.2$$

$$\Delta T_f = i \times K_f \times m = 1.2 \times 1.86 \times 0.5$$

$$= 1.116 \text{ K} = 1.12 \text{ K}$$

67.  $i = 1 + \left(\frac{1}{n} - 1\right) \alpha$

Here  $n = 2$  (dimer formation)

$$i = 0.54$$

On solving

$$\alpha = 0.92.$$

69. A Slightly soluble salt when dissolves in water and the temperature is increased then solubility of the salt increases.

70. Let the vapour pressure of pure ethyl alcohol be  $P$ ,

According to Raoult's law,

$$290 = 200 \times 0.4 + P \times 0.6$$

$$P = \frac{290 - 80}{0.6} = 350 \text{ mm Hg}$$

71.  $\frac{P^\circ - P_S}{P^\circ} = X_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1}$

$$= \frac{w_2/M_2}{w_1/M_1} / = \frac{18 \times 60}{100 \times 18}.$$

$$= \frac{18}{60} \times \frac{18}{100} = 0.05$$

72. Solutions with the same osmotic pressure are isotonic.

Let the molar mass of the substance be  $M$ .

$$\pi_1 = C_1 RT = C_2 RT = \pi_2$$

$$\text{So, } C_1 = C_2$$

As density of the solutions are same

$$\text{So } \frac{5.25}{M} = \frac{15}{60}$$

$$M = 5.25 \times 60 = 210$$

73.  $P_T = P_A^\circ X_A + P_B^\circ X_B$

$$760 = 520 X_A + P_B^\circ (1 - X_A)$$

On solving, we get

$$X_A = 0.5$$

So mole % of A = 50 %

74.  $P_{\text{total}} = P_A X_A + P_B X_B$

$$= 100 \times \frac{2}{5} + 80 \times \frac{3}{5}$$

$$= 88 \text{ torr}$$

75.  $\frac{P^\circ - P_S}{P_S} = X_{\text{solute}}$

$$\frac{17.5 - P_S}{P_S} = \frac{0.1}{10}$$

$$\frac{17.5 - P_S}{P_S} = 0.01$$

On solving, we get

$$P_S = 17.325 \text{ mm Hg.}$$

### Brainteasers Objective Type Questions



Initially	1	0	0
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at eq.	$(1 - 0.2) 0.2$	$0.2 \times 0.2$	$0.2 \times 0.2$
--------	-----------------	------------------	------------------

0.16 M	0.04 M	0.04 M
--------	--------	--------

total moles of solution at eq.

$$= 0.16 + 0.04 + 0.04$$

$$= 0.24$$

## 9.48 ■ Solutions and Colligative Properties

$$\text{As } \Delta T_f = K_f \cdot m$$

$$= 1.86 \times 0.24$$

$$= 0.45$$

$$\text{so f.p.} = 0 - \Delta T_f = 0 - 0.45$$

$$= -0.45^\circ\text{C}$$

78. Solution of sucrose is isotonic with solution of glucose, thus

$$P(\text{sucrose}) = P(\text{glucose})$$

$$\frac{n_s}{V_s} \cdot RT = \frac{n_g}{V_g}$$

$$\frac{n_s}{V_s} = \frac{n_g}{V_g}$$

$$\text{As } V_s = V_g = 1 \text{ litre}$$

$$\text{So } n_s = n_g$$

$$\frac{W_s}{(\text{mol wt.}) S} = \frac{W_g}{(\text{mol. wt.}) G}$$

$$\frac{34.2}{342} = \frac{x}{180}$$

$$x = 18.0 \text{ gm}$$

79. The depression in freezing point is proportional to molal concentration of the solute that is,

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m \text{ i or}$$

$$K_f = \Delta T_f \cdot i \times m$$

= constant

$$\text{So, } \frac{\Delta T_{f \text{ NaCl}}}{i \text{ NaCl} \times m \text{ NaCl}} = \frac{\Delta T_f}{i \times m}$$

= constant

$$\frac{0.37}{2 \times 0.01} = \frac{\Delta T_{f \text{ Urea}}}{0.02 \times 1} \Rightarrow$$

$$\frac{\Delta T_f}{0.02} = 0.37 \times 0.02$$

$$= 0.37^\circ\text{C}$$

80. Relative lowering of vapour pressure of an aqueous solution containing non-volatile solute is = mole fraction of solute

$$\text{As } \frac{P_0 - P_s}{P_0} = \frac{n}{n + N} = 0.0125$$

$$\Rightarrow \frac{n + N}{n} = \frac{1}{0.0125} \frac{N}{n} = \frac{1}{0.0125} - 1$$

$$= \frac{0.9875}{0.0125}$$

$$\text{So, } \frac{N}{n} = \frac{0.9875}{0.0125}$$

$$\text{Now, molality} = \frac{0.0125 \times 1000}{0.9875 \times 18} = 0.70$$

82. Since the two solutions have same molarity, so the value of O.P.  $\alpha$  i

$\text{NaNO}_3$  being a strong electrolyte,  $i = 2$ ,

But for  $\text{CH}_3\text{COOH}$  (weak electrolyte),

$$i = 1 + \alpha$$

$$i \text{ for } \text{NaNO}_3 > i \text{ for } \text{CH}_3\text{COOH}$$

since O.P.  $\propto i$ , therefore

$$\text{O.P. of } \text{NaNO}_3 (P_1) > \text{O.P. of } \text{CH}_3\text{COOH} (P_2)$$

83. Given that

$$nx = ny = 1 \text{ or } \frac{nx}{ny} = 1$$

$$\text{As, } x_x = \frac{1}{1+1} = \frac{1}{2} = 0.5$$

$$x_y = \frac{1}{2} = 0.5$$

$$P = P_x^0 x_x + P_y^0 x_y = 00$$

$$\text{or } P = 0.5 P_x^0 + 0.5 P_y^0 = 400 \dots (\text{i})$$

$$\text{When } \frac{nx^1}{ny^1} = \frac{1}{2} \text{ at same temperature}$$

$$\text{Then } x_x^1 = \frac{1}{3} \text{ & } x_y^1 = \frac{2}{3}$$

$$\text{So, } P = P_x^0 x_x^1 + P_y^0 x_y^1 = 350 \dots (\text{ii})$$

$$P = \frac{1}{3} P_x^0 + \frac{2}{3} P_y^0 = 350$$

Solving equation (i) and (ii), we get

$$P_x^0 = 550 \text{ and } P_y^0 = 250.$$

$$84. \pi = \frac{W_2 \cdot RT}{M_2} = \frac{4 \times 0.082 \times 300}{246 \times 1}$$

$$\pi = 0.4 \text{ atm}$$

85. Benzoic acid exists as a dimer because of hydrogen bonding.

$$88. \frac{p^o - ps}{p} = \frac{W_2}{M_2} \times \frac{M_1}{W_1}$$

$$M_2 = \frac{W_2 \cdot M_1}{(p^o - ps/p^o) \cdot W_1}$$

$$= \frac{5 \times 18}{(3000 - 2985/3000) \times 100}$$

On solving,

$$M_2 = 180.$$

$$89. K_f = \frac{RT_f^2}{100 I_f}; K_b = \frac{RT_b^2}{1000 I_v}$$

$$T_f = 289.6; T_b = 391.3$$

$$\frac{K_f}{K_b} = \frac{(289.6)^2 I_v}{(391.3)^2 I_f} = \frac{3.57}{3.07} = 1.163$$

$$\frac{I_v}{I_f} = 1.163 (391.3/289.6)^2 = 2.12$$

90. 33% aq. solution by weight means 33 g of  $\text{NH}_3$  in 100 g of solution that is, 33 / 17 mole of  $\text{NH}_3$  per 67 g of water.

$$\text{So molality of solution} = \frac{33}{17} \times \frac{1000}{67} = 28.97$$

$$\text{Volume of 100 g of solution} = \frac{100}{0.892} \text{ cm}^3$$

$$= 112.1 \text{ cm}^3$$

So molarity of the solution

$$= \frac{33}{17} \times \frac{1000}{112.1} = 17.31$$

$$91. \Delta T_b = K_b \cdot m = 0.51 \times 0.1 = 0.051^\circ$$

$$\text{now b.p. of solution} = 100 + \Delta T_b$$

$$= 100 + 0.051$$

$$= 100.051^\circ\text{C}$$

92. Number of ions formed



$$0.01 \text{ mole} : 0.01 \times 2 \text{ mole} : 0.01 \times 3 \text{ mole}$$

$$1 : 2 : 3$$

Thus  $\Delta T_f$  is also in the same ratio

( $\Delta T_f \propto i$  when molality is constant)

$$93. \pi = CRT$$

$$C = \frac{\pi}{RT} = \frac{0.0821}{0.0821 \times 300}$$

$$= 0.3 \times 10^{-2} \text{ mol L}^{-1}$$

96. Except glucose, all other are electrolytes undergoing dissociation ( $i > 1$ ). Glucose is non electrolyte,  $i = 1$ , so it has least value of  $\Delta T_f$  and f.p. is maximum.

$$97. \text{Wt. of sugar solution} = 214.2 \text{ g}$$

$$\text{Wt. of sugar} = 34.2 \text{ g}$$

$$\text{Wt. of water} = 214.2 - 34.2 = 180 \text{ g}$$

$$\text{Molality} = W2/M2 \times 1000 \times W1$$

$$= 34.2/342 \times 1000/180 = 0.55 \text{ m}$$

$$98. N_1 V_1 + N_2 V_2 + N_3 V_3 = N_4 V_4$$

$$1 \times 5 + \frac{1}{2} \times 20 + \frac{1}{3} \times 30 = N4 \times 1000$$

$$5 + 10 + 10 = N_4 \times 1000$$

On solving, we get

$$N_4 = \frac{25}{1000} = \frac{1}{40}.$$

$$99. I = \frac{1}{2} (m_1 z_1^2 + m_2 z_2^2 + \dots)$$

Here,  $m$  = molality of the ion

$z$  = its valency

$$m(\text{K}^+) = 0.1, z(\text{K}^+) = 1$$

$$m(\text{Cl}^-) = 0.1, z(\text{Cl}^-) = 1$$

$$m(\text{Cu}^{2+}) = 0.2, z(\text{Cu}^{2+}) = 2$$

$$m(\text{SO}_4^{2-}) = 0.2, z(\text{SO}_4^{2-}) = 2$$

So

$$I = \frac{1}{2} [0.1 \times 1^2 + 0.1 \times 1^2 + 0.2 \times 2^2 + 0.2 \times 2^2]$$

$$= 0.9.$$

$$100. \pi = \frac{W}{M} RT$$

$$M = \frac{0.082 \times 300 \times 50}{4.11} = 300$$

This is the apparent molecule weight.

$$i = \frac{M_{\text{nor}}}{M_{\text{apparent}}} = \frac{180}{300} = \frac{3}{5} = 0.6$$

## 9.50 ■ Solutions and Colligative Properties

As  $i = 1 + \alpha (1/n - 1)$

here  $n = 2$ ,  $\alpha$  = degree of dissociation

So  $0.6 = 1 + \alpha (-\frac{1}{2})$

$\frac{1}{2} \alpha = 0.4$

$\alpha = 0.8$  or 80%

$$101. M_2 = \frac{1000 K_f w_2}{w_1 \Delta T_f}$$

$$= \frac{1000 w_2}{w_1 \Delta T_f} \times \frac{RT_0^2}{1000 L_f}$$

$$= \frac{1000 \times 2.423}{100 \times 0.661} \times 2 \times \frac{(353.1)2}{1000 \times 35.7}$$

$$= 256 \text{ g mol}^{-1}$$

If  $S_x$  is the formula, then molecular mass

$$X \times 32 = 56$$

$$X = 8.$$

$$102. X_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{w_1 / M_1 + n_2}$$

(If  $w_1 = 1000 \text{ g}$ ,  $n_2 = \text{molality (m)}$ ).

For  $C_6H_6$ ,  $M_1 = 78$

So,

$$\frac{m}{1000/78 + m} = 0.2$$

$$m = 0.2 [(1000/78) + m]$$

$$0.8 m = 2.56$$

$$m = 2.56/0.8 = 3.2$$

103. Boiling point

$$= T_0 (\text{solvent}) + \Delta T_b (\text{elevation in b.p.})$$

$$\Delta T_b = mi K_b$$

where,  $m$  is the molality ( $\approx$  molarity  $m$ )

$i$ , the vant Hoff factor  $= [1 + (y - 1)x]$

$K_b$ , molal elevation constant.

Thus  $\Delta T_b \propto i$

Assume 100 % ionization

$$A. mi(Na_2SO_4) = 0.01 [1 + (y-1)x] = 0.03$$

$$B. mi(KNO_3) = 0.01 \times 2 = 0.02$$

$$C. mi(\text{urea}) = 0.015$$

$$D. mi(\text{glucose}) = 0.015$$

104. Since the two solution are isotonic, thus

$$\frac{W_2 \text{ (glycerine)}}{M_2 \cdot V_2} = \frac{W_2 \text{ (glucose)}}{M_2 \cdot V_2}$$

$$\frac{1.03}{M_2 \times 0.1} = \frac{2}{180 \times 0.1}$$

$$\text{or } M_2 = \frac{1.03 \times 180 \times 0.1}{0.1 \times 2} = 92.7$$

105. Since  $HNO_3$  is monobasic, molarity = 1M

Since  $H_2SO_4$  is dibasic, molarity = normality/basicity =  $1/2 = 0.5 \text{ M}$

Now, 1M  $HNO_3$  give 2 mole of ions in aqueous solution and 0.5 M  $H_2SO_4$  give  $3 \times 0.5 = 1.5$

Mole of ions in aqueous solution.

$\Delta T_b \propto$  no. of ions

$\Delta T_b$  is more for  $HNO_3$  and therefore b.p. is more for  $HNO_3$  solution.

$$106. K_f \text{ for water} = \frac{\Delta T_f \times W \times m}{1000 \times w}$$

(here  $W$  = wt. of water,  $w$  = wt. of cane sugar,  $m$  = molecular wt. of cane sugar)

$$= \frac{2.15 \times 100 \times 342}{1000 \times 5} = 14.7$$

for 5% glucose

$$\Delta T_f = \frac{K_f \times 1000 \times w}{W \times m}$$

$$= \frac{14.7 \times 1000 \times 5}{100 \times 180} = 4.08$$

freezing point of glucose solution

$$= 273.15 - 4.08 = 269.07 \text{ K}$$

107. As  $K_f = 105 \Delta T_f$

$$\Delta T_f = \frac{1}{105} \times K_f$$

$$\Delta T_f = \text{Molality} \times K_f$$

$$\text{Molality} = 1/105 = 0.0095$$

Molecular mass of urea ( $NH_2CONH_2$ ) = 60

So amount of urea to be dissolved

$$= 0.0095 \times 60 = 0.57 \text{ g}$$

108.  $n(P) = 3, n(Q) = 2$

$$p^o(P) = 80 \text{ torr}, p^o(Q) = 60 \text{ torr}$$

$$x(P) = 3/5, x(Q) = 2/5$$

$$p(P) = 3/5 \times 80 = 48 \text{ torr}$$

$$p(Q) = 2/5 \times 60 = 24 \text{ torr}$$

$$p(\text{Total}) = p(P) + p(Q)$$

$$= 48 + 24 = 72 \text{ torr}$$

111.  $K_b = \frac{RT^2}{L_v \times 1000}$

$$\left( L_v = \frac{9800}{18} = 544.44 \text{ cal/g} \right)$$

$$K_b = \frac{2\text{cal} \times (373)^2}{544.44 \times 1000} = 0.511^\circ$$

112. For original solution,  $\pi V_1 = \frac{W_2}{M_2} S.T.$

$$\frac{500}{760} \times V_1 = \frac{W_2}{M_2} \times S \times 283 \quad \dots \dots \dots \text{(i)}$$

After dilution,

$$\frac{105.3}{760} \times V_2 = \frac{W_2}{M_2} \times S \times 298 \quad \dots \dots \text{(ii)}$$

$$\text{Now } \frac{V_2}{V_1} \times \frac{105.3}{760} = \frac{298}{283}$$

$$\text{Or } \frac{V_2}{V_1} = \frac{298}{283} \times \frac{500}{105.3} = 5$$

Thus, the solution is diluted to five times its original volume.

113. As  $\Delta T_f = \frac{i K_f w \times 1000}{W \times M}$

On putting the values and solving  $i = 0.95$

As 'i' is less than 1 so no dissociation is possible  
Hence  $\alpha = 0$

114.  $7 \text{ g L}^{-1} \text{ MgCl}_2 = \frac{7}{24 + 71} \text{ mol L}^{-1}$

$$= \frac{7}{95} \text{ mol L}^{-1}$$

$$= \frac{7 \times 3}{95} \text{ mol L}^{-1} \text{ of ions} = 0.22$$

$$7 \text{ g L}^{-1} \text{ NaCl} = \frac{7}{23 + 35.5} \text{ mole}$$

$$= \frac{7}{58.5} \text{ mole}$$

$$= \frac{7 \times 2}{58.5} \text{ mol L}^{-1} \text{ of ions} = 0.24$$

As concentration of ions in NaCl solution is greater so NaCl solution (solution B) will have greater osmotic pressure.

115. In solution if  $X_A = X, X_B = 2X$  and if  $P_{A^o} = P, P_{B^o} = 2P$

$$\text{So } P_A = X \times P$$

$$P_B = 2X \times 2P = 4X \times P$$

$$P_{\text{total}} = 5XP$$

Mole fraction in vapour phase

$$= \frac{P_A}{P_{\text{total}}} = \frac{XP}{5XP} = \frac{1}{5} = 0.2$$

116. Loss in weight of solution  $\alpha$  V.P. of solution ( $P_s$ )

Loss in weight of solvent  $\alpha P_o - P_s$

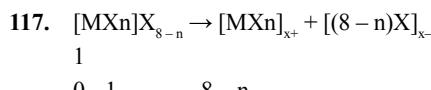
$$\frac{P_o - P_s}{P_s} = \frac{\text{Loss in wt. of solvent}}{\text{Loss in wt. of solution}}$$

$$= \frac{w_2/M_2 - w_1/M_1}{w_1/M_1 - w_2/M_2}$$

$$\frac{0.05}{2.5} = \frac{10/M_2}{90/18} = \frac{2}{M_2}.$$

On solving, we get

$$M_2 = 100$$



$$\text{As } \Delta T_f = i \times K_f \times m$$

$$\text{So } 0.0054 = i \times 1.86 \times 10^{-3}$$

$$i = \frac{0.0054}{1.86 \times 10^{-3}} = \frac{5.4}{1.86} = 2.9$$

$$i = 2.9 = 9 - n$$

$$n = 6.1 = 6.$$

So the complex is  $[MX_6]X_2$ .

## 9.52 ■ Solutions and Colligative Properties

118.  $mP = 0.1 \text{ g}$

$$M_p = 100, m_q = 0.1 \text{ g}, m_b = 100 \text{ g}$$

$$\Delta T_p = 0.4^\circ\text{C}, \Delta T_q = 0.2^\circ\text{C}$$

$$\Delta T_b = K \frac{w_A}{m_A w_B} .$$

Here  $K$  = molal elevation constant

$$w_A = \text{mass of solute}$$

$$m_A = \text{molar mass of solute}$$

$$w_B = \text{mass of solvent}$$

$$\frac{\Delta T_p}{\Delta T_q} = K \times \frac{(wP/MP wB)}{K \times (wQ/MQ wB)}$$

$$\frac{0.2}{0.4} = \frac{0.1}{100 \times 100} \times \frac{M_q \times 100}{0.1}$$

$$\frac{1}{2} = \frac{M_q}{100}$$

$$M_q = 50$$

So Ratio of molar weights of P and Q is 2 : 1.

119. For vapour phase:

$$X_A = \frac{P_A}{P_{\text{Total}}} \text{ or } X_B = \frac{P_B}{P_{\text{Total}}} .$$

$$(1 - X_A) = \frac{P_B}{P_{\text{Total}}} .$$

$$\frac{P_A}{P_B} = \frac{X_A}{(1 - X_A)} \quad \dots\dots(1)$$

For liquid phase:

$$P_A = P^o_A X_A$$

$$P_B = P^o_B X_B = P^o_B (1 - X_A)$$

$$\frac{P_A}{P_B} = \frac{60 \times 0.2}{15 (1 - 0.2)} = 1 \quad \dots\dots(2)$$

Comparing equation (1) and equation (2), we get

$$\frac{X_A}{(1 - X_A)} =$$

$$X_A = 0.5$$

120.  $\text{H}_2\text{SO}_4$  is 98 % by weight.

$$\text{Weight of H}_2\text{SO}_4 = 98 \text{ g}$$

Weight of solution = 100 g

$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{100}{1.80} \text{ ml} \\ = 55.55 \text{ ml} = 0.0555 \text{ L}$$

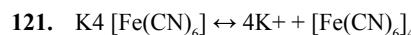
$$\text{Molarity of solution} = \frac{98}{98 \times 0.0555} \text{ M} \\ = 18.02 \text{ M}$$

Let  $V$  ml of this  $\text{H}_2\text{SO}_4$  are used to prepare one litre of 0.1 M  $\text{H}_2\text{SO}_4$ .

$$\text{mM of conc. H}_2\text{SO}_4 = \text{mM of dil. H}_2\text{SO}_4$$

$$V \times 18.02 = 1000 \times 0.1$$

$$V = \frac{1000 \times 0.1}{18.02} = 5.55 \text{ mL}$$



$$\begin{array}{cccc} \text{Initial conc.} & 1 & 0 & 0 \end{array}$$

$$\begin{array}{cccc} \text{At eqbm.} & 1 - \alpha & 4\alpha & \alpha \end{array}$$

$$i = 1 - \alpha + 4\alpha + \alpha = 1 + 4\alpha$$

$$\alpha = 50/100 = 0.5$$

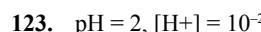
$$i = 1 + 4 \times 0.5 = 3$$

$$\pi = iCRT$$

$$= 3 \times 0.1 \times 0.0821 \times 300$$

$$= 7.389 \text{ atm.}$$

$$= 7.4 \text{ atm}$$



$$\begin{array}{cccc} \text{At start} & C & 0 & 0 \end{array}$$

$$\begin{array}{cccc} \text{At eqbm.} & C(1-\alpha) & C\alpha & C\alpha \end{array}$$

$$[\text{H}^+] = C\alpha$$

$$\text{or } \alpha = [\text{H}^+]/C = 10^{-2}/0.1 = 0.1$$

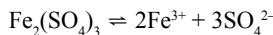
$$i = 1 + \alpha = 1 + 0.1 = 1.1$$

$$\text{now, } \pi = i \cdot \text{C.S.T}$$

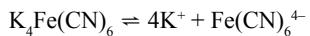
$$= 1.1 \times 0.1 \times \text{S.T.}$$

$$= 0.11 \text{ S.T.}$$

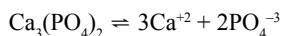
127. Osmotic pressure is a colligative property. Its value depends only on the number of entities in solution. Then



$$2 + 3 = 5 \text{ entities}$$



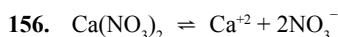
$$4 + 1 = 5 \text{ entities}$$



$$4 + 1 = 5 \text{ entities}$$

As they have the same molality and 'i' so they have same osmotic pressure.

129. Molarity decreases, volume increases with increase in temperature



Here n = 3

$$\alpha = 2$$

$$\text{As } \alpha = \frac{l - 1}{n - 1}$$

$$0.87 = \frac{l - 1}{3 - 1}$$

on solving

$$l = 2.74$$

$$162. \Delta T_f = K_f \times m = 2 \times \frac{0.1}{0.9 \times 46} \times 1000$$

$$\begin{aligned} \text{Freezing point of solution M, } T'_f &= T^o_f - \Delta T_f \\ &= 155.7 - 4.83 \end{aligned}$$

$$T'_f = 150.9 \text{ K}$$

163. Total vapour pressure

$$P = P^o A X_A \quad (\text{solute in nonvolatile here})$$

$$P = 40 \times 0.9 \quad (\text{vapour pressure of pure ethanol} = 40 \text{ mm of Hg})$$

$$= 36 \text{ mm of Hg}$$

$$164. \Delta T_b = K_b \times m = 0.52 \times \frac{0.1}{0.9 \times 18} \times 1000$$

$$\Delta T_b = \frac{520}{9 \times 18} = 3.20$$

The boiling point of the solution

$$T'_b = T^o_b + \Delta T_b$$

$$T'_b = 373 + 3.20 \quad (\text{standard B.P. of water} = 373 \text{ K})$$

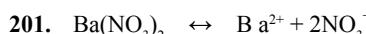
$$T'_b = 376.2 \text{ K}$$

170. The vapour pressure of 0.45 molar urea solution is equal to that of 0.45 molar solution of sugar.

172. The freezing point of 0.1 M urea is greater than that of 0.1 M KCl solution.

176. Elevation of boiling point increases with increasing the number of ions/molecule in the solution.

183. At 373 K (100°C), the vapour pressure of water is equal to 1 atmospheric pressure which is 1.013 bar.



$$\text{Initial} \quad 0.1 \text{ M} \quad 0 \quad 0$$

$$\text{At eq.} \quad (0.1 - \alpha) \text{ M} \quad \alpha \text{ M} \quad \alpha \text{ M}$$

$$i = \frac{(0.1 - \alpha) + \alpha + 2\alpha}{0.1}$$

$$= \frac{0.1 + 2\alpha}{0.1} = 2.74$$

on solving

$$\alpha = 0.087$$

$$\text{so } \alpha \% = \frac{0.087}{0.1} \times 100 = 87 \%$$

$$203. \alpha = 0.23$$

$$\text{as } i = 1 + \alpha = 1 + 0.23 = 1.23$$

now

$$n \text{ (moles of acetic acid)} = 3 \times 10 - 3 \times 103$$

$$60$$

$$= 0.05$$

molality = moles of acetic acid

wt. of solvent in kg

$$= 0.05 = 0.1$$

$$498.5 \times 1000$$

$$\text{As } \Delta T_f = i \cdot K_f \cdot m = 1.23 \times 1.86 \times 0.1$$

$$= 0.228 \text{ K}$$

$$204. \text{Eq. wt. of } (\text{COOH})_2 \cdot 2\text{H}_2\text{O} = 126/2 = 63$$

Normality of oxalic acid (N)

$$N = \frac{W}{E \times V} \times 1000$$

$$= 6.3/63 \times 1000/250 = 0.4 \text{ N}$$

## 9.54 ■ Solutions and Colligative Properties

(oxalic acid) ( $\text{NaOH}$ )

$$N_1 V_1 = N_2 V_2$$

$$0.4 \times 10 = 0.1 \times V_2$$

$$\text{so } V_2 = 40 \text{ Ml}$$

- 205.** At the freezing point, liquid and solid are in equilibrium. When a solution of a non-volatile solute is cooled to a temperature below the freezing point of solution, some of the liquid solvent will separate out as a solid solvent.

**206.**  $P(\text{Na}_2\text{SO}_4) = i CRT = i(0.004) RT$

$$P(\text{glucose}) = CRT = 0.010 RT$$

As solutions are isotonic,  $i(0.004) RT$

$$= 0.01 RT$$

this gives  $i = 2.5$



1 mole	0	0
--------	---	---

1 - $\alpha$	2 $\alpha$	$\alpha$ , total = 1 + 2 $\alpha$
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that is,  $i = 1 + 2\alpha$

$$\alpha = i - 1 = 2.5 - 1 = 1.5 = 0.75 = 75\%$$

2	2	2
---	---	---

- 207.**  $\text{CuCl}_2$  is an electrolyte which ionizes in solution as follows:



At t = 0	1 mole	0	0
----------	--------	---	---

After ionis.	(1 - $\alpha$ ) mole	$\alpha$ mole	2 $\alpha$ mole
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Number of particles after ionization

$$= 1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$$

Van't Hoff factor (i)

$$= \frac{\text{Number of particles after ionization}}{\text{Number of particles before ionization}}.$$

$$\text{Or (i)} = \frac{1 + 2\alpha}{1} \text{ (On 100% ionization } \alpha = 1)$$

$$= \frac{1 + 2 \times 1}{1} = 3$$

The elevation in boiling point (when colligative property is abnormal)

$$\Delta T_b = i \times K_b \times m$$

Here  $m$  = Molality of solution

Molality of  $\text{CuCl}_2$  solution

$$= \frac{\text{Weight of CuCl}_2 \text{ in gm}}{\text{Mol. weight of CuCl}_2}$$

$$= \frac{\text{Weight of water (solvent) in Kg}}{13.44/134.4} = 0.1 \text{ m}$$

$$\text{So } \Delta T_b = 3 \times 0.52 \times 0.1$$

$$= 0.156 \sim 0.16^\circ\text{C}$$

**208.**  $\Delta T_f = K_f \times \text{molality} \times i$

$$2 = 1.72 \times \frac{20}{172} \times \frac{1000}{50} \times i$$

$$i = 0.5.$$

**209.**  $P = K_H \times N_2$

$$0.8 \times 5 = 1 \times 10^5 \times N_2$$

$$X_{N_2} = 4 \times 10^{-5} \text{ (In 10 moles H}_2\text{O)}$$

$$\frac{X_{N_2}}{n_{N_2} + n_{H_2O}}$$

$$4 \times 10^{-5} = \frac{n_{N_2}}{n_{N_2} + 10}$$

On solving

$$n_{N_2} = 4 \times 10^{-4}$$

## Numericals for Practice

1. A solution of urea (mol mass 56 g mol<sup>-1</sup>) boils at 100.18°C at the atmosphere pressure. If K<sub>f</sub> and K<sub>b</sub> for water are 1.86 and 0.512 K kg mol<sup>-1</sup> respectively, the above solution will freeze at  
 a. 6.54°C      b. -6.54°C  
 c. -0.654°C      d. 0.654°C
2. How many moles of Fe<sup>2+</sup> ions are formed when excess iron is treated with 500 mL of 0.4 N HCl under inert atmosphere? Assume no change in volume.  
 a. 0.4      b. 0.1  
 c. 0.2      d. 0.8
3. Two liquids having vapour pressures P<sub>A</sub><sup>o</sup> and P<sub>B</sub><sup>o</sup> in pure state in the ratio of 2 : 1 are mixed in the molar ratio of 1 : 2. The ratio of their moles in the vapour state would be  
 a. 1 : 1      b. 2 : 1  
 c. 1 : 2      d. 1 : 3
4. The molar heat of vapourisation of water at 100°C is 40.584 kJ/mole. Find the temperature at which a solution having 5.6 gm of glucose in 1 litre of water boil  
 a. 200.32°C      b. 100.16°C  
 c. 98.36°C      d. 90°C
5. The density (in g ml<sup>-1</sup>) of a 3.60 M sulphuric acid solution that is 29% H<sub>2</sub>SO<sub>4</sub> (molar mass = 98 g mol<sup>-1</sup>) by mass will be  
 a. 1.88      b. 1.22  
 c. 1.45      d. 1.64
6. A solution of a non-volatile solute in water has a boiling point of 102.3°C. The vapour pressure of water above this solution at 65°C K is [given: p<sub>0</sub> (water) = 0.2467 atm at 65°C and K<sub>b</sub> for water = 0.52 K kg mol<sup>-1</sup>]  
 a. 0.23 atm      b. 0.46 atm  
 c. 0.115 atm      d. 0.32 atm
7. The vapour pressure of pure water at 298 K is 23.86 mm. The vapour pressure of a solution of sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) in 5.66 moles of water is 23.492 mm Hg. The mass of sucrose in the solution is  
 a. 14.25 g      b. 29.85 g  
 c. 38.65 g      d. 35 g
8. 1 m solution of a carboxylic acid in solvent Benzene shows an elevation of boiling point 1.5178 K.
- The degree of association of the acid in Benzene is? (K<sub>b</sub> = 2.53 K kg mol<sup>-1</sup>)  
 a. 80%      b. 60%  
 c. 70%      d. 65%
9. Certain mass (Wg), of urea was dissolved in 500 g of water and cooled upto -0.5°C whereby 128 g of ice separates out from the solution. If cryoscopic constant for water be 1.86 C m<sup>-1</sup>, the value of W will be  
 a. 3 g      b. 6 g  
 c. 12 g      d. 0.6 g
10. Elevation in boiling point of an aqueous urea solution is 0.52° (K<sub>b</sub> = 0.52° mol<sup>-1</sup> kg). Hence, mole fractions of urea and water in this solution are respectively:  
 a. 0.0176, 0.9824  
 b. 0.9824, 0.0176  
 c. 0.0186, 0.9814  
 d. 0.9814, 0.0186
11. Two solutions of a substance (non-electrolyte) are mixed in the following manner. 480 mL of 1.5 M first solution +520 mL of 1.2 M second solution. What is the molarity of the final mixture?  
 a. 1.344 M      b. 2.70 M  
 c. 1.50 M      d. 1.20 M
12. A 5% solution (by mass) of cane sugar in water has freezing point of 271 K and freezing point of pure water is 273.15 K. The freezing point of a 5% solution (by mass) of glucose in water is  
 a. 271 K      b. 273.15 K  
 c. 269.07 K      d. 277.23 K
13. Benzene and toluene form nearly ideal solutions. At 20°C, the vapour pressure of benzene is 75 torr and that of toluene is 22 torr. The partial vapour pressure of benzene at 20°C for a solution containing 78 g of benzene and 46 g of toluene in torr is  
 a. 25      b. 50  
 c. 37.5      d. 53.5
14. The van't Hoff factor for 0.1 M Ba(NO<sub>3</sub>)<sub>2</sub> solution is 2.74. The degree of dissociation is  
 a. 91.4%      b. 87%  
 c. 100%      d. 75%

## 9.56 ■ Solutions and Colligative Properties

15. A solution of urea (mol mass 56 g mol<sup>-1</sup>) boils at 100.18°C at the atmosphere pressure. If  $K_f$  and  $K_b$  for water are 1.86 and 0.512 K kg mol<sup>-1</sup> respectively, the above solution will freeze at  
 a. 6.54°C      b. -6.54°C  
 c. -0.654°C      d. 0.654°C
16. The van't Hoff factor for BaCl<sub>2</sub> at 0.01 M concentration is 1.98. The percentage dissociation of BaCl<sub>2</sub> at this concentration is  
 a. 69      b. 49  
 c. 98      d. 89  
 e. 106
17. Two liquids A and B forming an ideal solution has a total vapour pressure of 900 mm Hg at 20°C. The mole fraction of A in the liquid mixture is 0.5. If the vapour pressure of pure B is twice that of pure A, the partial pressure of A in the vapour phase is  
 a. 100 mm      b. 150 mm  
 c. 600 mm      d. 300 mm
18. Adrenaline is the hormone that triggers release of extra glucose molecules in times of stress or emergency. A solution of 0.64 g of adrenaline in 36.0 g of CCl<sub>4</sub> causes an elevation of 0.49°C in the boiling point. What is the molar mass of adrenaline?  
 a.  $1.8 \times 10^2$       b.  $3.6 \times 10^2$   
 c.  $1.8 \times 10^3$       d.  $3.6 \times 10^3$
19. A decimolar solution of pot. ferrocyanide is 50% dissociated at 300 K. calculate the osmotic pressure of the solution ( $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ )  
 a. 0.07389 atm      b. 7.389 atm  
 c. 738.89 atm      d. 73.89 atm
20. Molarity of liquid HCl if density of solution is 1.17 g/cc, is  
 a. 32.05      b. 12.15  
 c. 3.05      d. 22.10
21. How many grams of urea should be dissolved in 100 g water in order to produce a solution with a 105°C difference between the freezing point and the boiling point? ( $K_f = 1.86 \text{ C m}^{-1}$ ,  $K_b = 0.52 \text{ }^\circ\text{C m}^{-1}$ )  
 a. 12.6 g      b. 1.26 g  
 c. 25.2 g      d. 6.3 g
22. The molality of 1 litre solution of 92% H<sub>2</sub>SO<sub>4</sub> (W/V) having density 1.84 g/ml is  
 a. 10.20      b. 1.02  
 c. 0.102      d. 5.122
23. A mixture of solid NaCl and solid sucrose, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, has an unknown composition. What 15.0 g of the mixture is dissolved in enough water to make 500 ml of solution, the solution exhibits an osmotic percentage of NaCl in the mixture?  
 a. 16.4%      b. 81.3%  
 c. 18.7%      d. 83.6%
24. An aqueous solution having 0.245 g of a solute in 20 g of H<sub>2</sub>O froze at -0.42°C. Find the molecular weight of solute. Here enthalpy of fusion of ice at 0°C is 6024.5 Joule mole<sup>-1</sup>?  
 a. 52      b. 63.56  
 c. 55      d. 61.24
25. A slow stream of dry air was passed through an aqueous solution containing 50 g (per litre) of a non-volatile substance in a vessel and then through pure water at the same temperature. The first vessel lost 0.4873 g in weight and the second 0.0127 g during the experiment. The molecular weight of the non-volatile solute is approximately  
 a. 18      b. 36  
 c. 32      d. 42
26. An aqueous solution of sucrose, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, containing 34.2 g/lit has an osmotic pressure of 2.38 atmospheres at 17°C for an aqueous solution of glucose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> to be isotonic with this solution, it would have  
 a. 18.0 g/lit  
 b. 16.2 g/lit  
 c. 36.6 g/lit of glucose  
 d. 14.0 g/lit
27. Density of a 2.05 M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is  
 a. 1.14 mol kg<sup>-1</sup>  
 b. 3.28 mol kg<sup>-1</sup>  
 c. 2.28 mol kg<sup>-1</sup>  
 d. 0.44 mol kg<sup>-1</sup>
28. Elements X and Y combine to form two compounds having molecular formula XY<sub>2</sub> and XY<sub>4</sub>. When dissolved in 20 g of benzene, 1 g XY<sub>2</sub> lowers the freezing point by 2.3°C and 1 g XY<sub>4</sub> lowers the freezing point by 1.3°C. If the cryoscopic constant for benzene be 5.1 K kg mol<sup>-1</sup>, the atomic mass of Y is  
 a. 35.44      b. 21.32  
 c. 36.96      d. 42.64

29. A solution is formed by dissolving 10.0 g of KCl in 500.0 g of H<sub>2</sub>O. What is the vapour pressure of the solution at 25°C if the vapour pressure of pure H<sub>2</sub>O is 23.8 mm Hg at 25°C?
- a. 47.2 ml      b. 23.6 ml  
c. 16.8 ml      d. 18.6 ml
30. The molal lowering of vapour pressure for water at its normal boiling point is
- a. 13.44 mm Hg  
b. 3.44 mm Hg  
c. 26.88 mm Hg  
d. 6.88 mm Hg

ANSWER KEYS	Q.	Ans.								
	1.	c	2.	b	3.	c	4.	b	5.	b
	6.	a	7.	b	8.	a	9.	b	10.	a
	11.	a	12.	c	13.	b	14.	b	15.	c
	16.	b	17.	d	18.	a	19.	b	20.	a
	21.	a	22.	a	23.	c	24.	c	25.	b
	26.	a	27.	c	28.	d	29.	b	30.	a

## Hints and Explanations

1.  $\Delta T_b = 100.18 - 100 = 0.18$

$$\frac{\Delta T_b}{\Delta T_f} = \frac{K_b m}{K_f m} = \frac{K_b}{K_f}$$

$$\frac{0.18}{\Delta T_f} = \frac{0.512}{1.86}$$

$$\Delta T_f = \frac{0.18 \times 1.86}{0.512} = 0.654$$

$$T_f = (0 - 0.654)^\circ C = -0.654^\circ C$$



Moles of Fe<sup>2+</sup> formed

$$= \frac{1}{2} \times \text{moles of HCl used}$$

$$= \frac{0.4 \times 500}{1000} = 0.1$$

5. Let the density of solution be 'd'

Molarity of solution given = 36

1 litre of solution contains 3.6 moles of H<sub>2</sub>SO<sub>4</sub>

1 litre of solution contains  $3.6 \times 98$  grams of H<sub>2</sub>SO<sub>4</sub>

As the solution is 29% by mass.

100 g solution contains 29 gm H<sub>2</sub>SO<sub>4</sub>

100/d ml solution contains 29 g of H<sub>2</sub>SO<sub>4</sub>

1000 ml solution contains  $3.6 \times 98$  g of H<sub>2</sub>SO<sub>4</sub>

$$3.6 \times 98 = \frac{29 \times d}{100} \times 1000$$

$$d = 1.22$$

6.  $\Delta T_f = K_b \times m$

$$2.3 = 0.52 \times m$$

$$m = 4.42$$

$$m = \frac{1 - X_A}{X_A} \times \frac{1000}{18}$$

On solving  $X_A = 0.926$

## 9.58 ■ Solutions and Colligative Properties

Hence  $P = P^o \times X_A$

$$= 0.2467 \times 0.926 = 0.228 = 0.23 \text{ atm}$$

7.  $\frac{23.86 - 23.492}{23.86} = \frac{w}{342 \times 5.66}$

$$w = 29.85 \text{ g.}$$

9. 128 g of ice separated means weight of solvent in liquid state = 500 – 128

$$= 372 \text{ g}$$

$$\text{As } \Delta T_f = K_f m$$

$$0 - (-0.5) = \frac{1.86 \times W}{60 \times 372} \times 1000$$

On solving, we get

$$W = 6 \text{ g.}$$

10.  $\Delta T_b = \text{molality} \times K_b$

$$0.52 = m \times 0.52$$

$$\text{Molality} = 1 \text{ mol kg}^{-1}$$

$$\text{So urea} = 1 \text{ mol}$$

$$\text{Water} = \frac{1000}{18} = 55.55$$

$$\text{Mole fraction of urea} = \frac{1}{56.55} = 0.0176$$

$$\text{Mole fraction of water} = 1 - 0.0176$$

$$= 0.9824$$

11.  $M_1 V_1 + M_2 V_2 = M_3 V_3$

(1<sup>st</sup> sol) (2<sup>nd</sup> sol) (mixture)

$$1.5 \times 480 + 1.2 \times 520 = M_3 (480 + 520)$$

$$1000 M_3 = 720 + 624$$

$$M_3 = 1344/1000 = 1.344 \text{ M}$$

12.  $K_f \text{ for water} = \frac{\Delta T_f \times W \times m}{1000 \times w}$

(here W = wt. of water, w = wt. of cane sugar, m = molecular wt. of cane sugar)

$$= \frac{2.15 \times 100 \times 342}{1000 \times 5} = 14.7$$

for 5% glucose

$$\Delta T_f = \frac{K_f \times 1000 \times w}{W \times m}$$

$$= \frac{14.7 \times 1000 \times 5}{100 \times 180} = 4.08$$

freezing point of glucose solution

$$= 273.15 - 4.08 = 269.07 \text{ K}$$

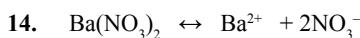
13.  $P_B = P_B^o X_B$

$$P_B^o = 75 \text{ torr}$$

$$X_B = \frac{78/78}{(78/78) + (46/92)} = \frac{1}{1 + 0.5} = \frac{1}{1.5}$$

$$P_B = 75 \times 1 = 50 \text{ torr}$$

$$1.5$$



Initial	0.1 M	0	0
---------	-------	---	---

At eq.	(0.1 - α) M	α M	α M
--------	-------------	-----	-----

$$i = \frac{(0.1 - \alpha) + \alpha + 2\alpha}{0.1}$$

$$= \frac{0.1 + 2\alpha}{0.1} = 2.74$$

on solving

$$\alpha = 0.087$$

$$\text{so } \alpha \% = \frac{0.087}{0.1} \times 100 = 87 \%$$

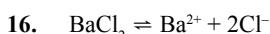
15.  $\Delta T_b = 100.18 - 100 = 0.18$

$$\frac{\Delta T_b}{\Delta T_f} = \frac{K_b m}{K_f m} = \frac{K_b}{K_f}$$

$$\frac{0.18}{\Delta T_f} = \frac{0.512}{1.86}$$

$$\Delta T_f = \frac{0.18 \times 1.86}{0.512} = 0.654$$

$$T_f = (0 - 0.654)^\circ\text{C} = -0.654^\circ\text{C}$$



Initial	1 mole	0	0
---------	--------	---	---

After	1 - α	α	2α
-------	-------	---	----

disso.

$$\text{Total} = 1 + 2\alpha$$

$$i = 1 + 2\alpha$$

$$\begin{aligned}\alpha &= \frac{i-1}{2} = \frac{1.98-1}{2} \\ &= \frac{0.98}{2} = 0.49 = 49\%\end{aligned}$$

17.  $x_A p_A^o + x_B p_B^o = 900$

$$0.5 p_A^o + 0.5 p_B^o = 900$$

$$0.5 p_A^o + 0.5 \times 2 p_A^o = 900$$

$$(\text{since } p_B^o = 2p_A^o)$$

$$\text{so } 1.5 p_A^o = 900$$

$$p_A^o = 900/1.5 = 600 \text{ mm}$$

Partial pressure of A (in the vapour phase) =  $0.5 \times 600 = 300 \text{ mm}$ .

19.  $K_4 [Fe(CN)_6] \leftrightarrow 4K^+ + [Fe(CN)_6]^{4-}$

Initial conc.	1	0	0
---------------	---	---	---

At eq.	$1 - \alpha$	$4\alpha$	$\alpha$
--------	--------------	-----------	----------

$$i = 1 - \alpha + 4\alpha + \alpha = 1 + 4\alpha$$

$$\alpha = 50/100 = 0.5$$

$$i = 1 + 4 \times 0.5 = 3$$

$$\pi = iCRT$$

$$= 3 \times 0.1 \times 0.0821 \times 300$$

$$= 7.389 \text{ atm.}$$

20. As 1 c.c. of the HCl solution contains

$$= 1.17 \text{ gm of HCl}$$

So 1000 c.c. of HCl solution will contain

$$= \frac{1.17 \times 1000}{1}$$

$$= 1170 \text{ gm of HCl}$$

Hence 36.5 g of HCl in 1000 c.c. = 1 M

$$\text{So } 1170 \text{ gm of HCl in 1000 c.c.} = \frac{1170}{36.5}$$

$$= 32.05 \text{ M}$$

21. Suppose weight of urea dissolve is X g.

$$T_f - T_b = 105^\circ\text{C}$$

$$0 - (-T_b) = 1.86 \times \frac{X}{100 \times 60} \times 1000 \quad \dots\dots(i)$$

$$T_b - 100 = 0.52 \times \frac{X}{100 \times 60} \times 1000 \quad \dots\dots(ii)$$

On subtracting equation (ii) from equation (i), we get

$$X = 12.6 \text{ g.}$$

22. 92%  $H_2SO_4$  (W/V) means 92 g of  $H_2SO_4$  is present in 100 cc of solution.

since vol. of solution = 1000 mL

Amount of  $H_2SO_4$  = 920 g per litre

$$d = 1.84 \text{ g/ml}$$

$$d = \frac{M}{V} \text{ or}$$

$$M = d \times V$$

$$= 1.84 \times 1000$$

$$= 1840 \text{ g}$$

$$\text{Wt. of solvent} = 1840 - 920 = -920 \text{ g}$$

$$\text{Molality} = \frac{920}{98} \times \frac{1000}{920} = 10.20 \text{ mm}$$

23. As  $M = \frac{\pi}{RT} = \frac{6.41}{298 \times 0.082}$

$$= 0.262 \text{ M}$$

There are 0.262 mol of particles per litre of solution and 0.131 mol particles in 500 mL. Each mole of sucrose provides 1 mol of particles and each mole of NaCl provides 2.

$$\text{Let } X = \text{g } C_{12}H_{22}O_{11}, 15.0 - X = \text{g NaCl}$$

$$\frac{X \text{ g } C_{12}H_{22}O_{11}}{342.3 \text{ g } C_{12}H_{22}O_{11}} + \frac{2(15.0 - X)}{58.44 \text{ g NaCl}}$$

$$= 0.131$$

$$58.44 X + 2(342.3)(15.0 - X)$$

$$= 0.131 (58.44)(342.3)$$

$$= 58.44X - 684.6X + 10,269 = 2,621$$

## 9.60 ■ Solutions and Colligative Properties

$$-626.2X = -7648; X = 12.2 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}$$

$$\frac{12.2 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}{15.0 \text{ g mixture}} \times 100$$

= 81.3% Sucrose

Hence % of NaCl = 10 – 81.3

= 18.7%

25.  $0.4873 \text{ g } \alpha \text{ p}$

$$0.0127 \text{ g } \alpha \text{ p}^\circ - p$$

$$\text{so } p \propto (0.4873 + 0.0127) \text{ g}$$

$$\text{Thus } \frac{p_o - p}{p_o} = x_2 = \frac{0.0127}{0.5} = 0.0254$$

$$x_2 = n_2/n_1$$

$$0.0254 = \frac{50 M}{55.56} = \frac{0.9}{M}$$

$$M = \frac{0.9}{0.0254} = 35.43 = 36$$

26. Solution of sucrose is isotonic with solution of glucose, thus

$$P(\text{sucrose}) = P(\text{glucose})$$

$$\frac{nS \cdot RT}{vS} = \frac{nG}{vG}$$

$$\frac{nS}{vS} = \frac{nG}{vG}$$

As  $vS = vG = 1 \text{ litre}$

$$\text{So } nS = nG$$

$$\frac{WS}{(\text{mol wt.})S} = \frac{WG}{(\text{mol. wt.})G}$$

$$\frac{34.2}{342} = \frac{x}{180}.$$

$$x = 18.0 \text{ gm}$$

27. Molarity,  $m = \frac{M}{1000d - MM_2} \times 1000$

where  $M$  = molarity,  $d$  = density,

$M_2$  = molecular mass

$$M = \frac{2.05}{1000 \times 1.02 - 2.05 \times 60} = 2.28 \text{ mol kg}^{-1}$$

28.  $M = \frac{K_f \times w \times 1000}{W \times \Delta T_f}$

Molecular weight of  $\text{XY}_2$

$$= \frac{5.1 \times 1 \times 1000}{2.3 \times 20} = 110.86$$

Molecular weight of  $\text{XY}_4$

$$= \frac{5.1 \times 1 \times 1000}{1.3 \times 20} = 196.15$$

Atomic mass of element Y

$$= \frac{196.15 - 110.86}{2} = 42.64 \text{ g mol}^{-1}$$

30. According to Raoult's law,

$$P_o - P_s = P_o \left( \frac{n}{N+n} \right)$$

For molal lowering  $n = 1$  mole

$$N = \frac{1000}{18} = 55.55 \text{ mole}$$

Vapour pressure of water at  $100^\circ\text{C}$

$$= 760 \text{ mm of Hg.}$$

Molal lowering in vapour pressure,

$$P_o - P_s = \frac{1}{1 + 55.55} \times 760$$

$$= 13.44 \text{ mm of Hg}$$

# CHAPTER 10

# Surface Chemistry

## Chapter Contents

Elementary concepts of adsorption (excluding adsorption isotherms); Colloids: types, methods of preparation and general properties; Elementary ideas of emulsions, surfactants and micelles (only definitions and examples) and Various levels of multiple-choice questions.

### ADSORPTION

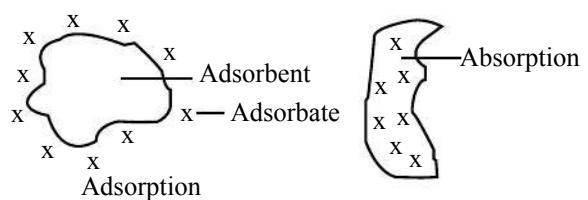
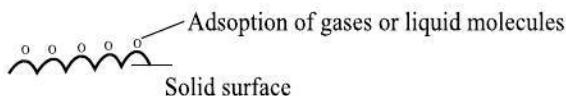
Adsorption is the phenomenon of higher concentration at surface brought about by the action of surface forces.

Or

It is change in the concentration in the interfacial layers between two faces of the system.

Or

The tendency of accumulation of molecular species at the surface than in the bulk of a solid is called adsorption.



Adsorption was introduced by Scheele during the discovery of uptake of gases by Charcoal and adsorption was developed by Kayser and Raymonds.

### Adsorbent

It is the substance on which another substance is adsorbed. It is also called interface. Example, solid  $\text{Al}_2\text{O}_3$ , charcoal, silica gel, clay metals in finely divided state etc.

## Adsorbate

It is the substance which is adsorbed on adsorbent.

## Features of Adsorption

- It is highly specific and selective in nature.
- It is a spontaneous process as  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$  are negative and characterized by decrease of enthalphy as well as decrease of entropy.
- It is a fast and an exothermic process.

Example, Silica gel adsorbs  $H_2O$

Inert gases  $CO_2$ ,  $NH_3$ ,  $Cl_2$ ,  $SO_2$  are also adsorbed on charcoal.

Dyes on animal charcoal

Air becomes dry (moisture free) on silica gel.

## ABSORPTION

It occurs inside the surface and a slower process. It is endothermic ( $\Delta H$  is positive) by nature.

Example, anhydrous  $CaCl_2$  absorbs water.

- According to Mc Bain, when adsorption and absorption occur simultaneously it is called sorption.

For example, uptake of gasses by zeolite.

## Positive and Negative Adsorption

In positive adsorption, the concentration of the adsorbate is more on the surface of the adsorbent than in the bulk while in negative adsorption the concentrations of the adsorbate is less relative to its concentration in the bulk.

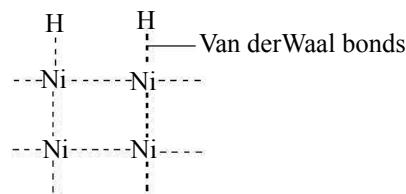
## Occlusion

The adsorption of gases on the surface of a metal is known as occlusion. Example,  $H_2$  gas on palladium surface.

## Desorption

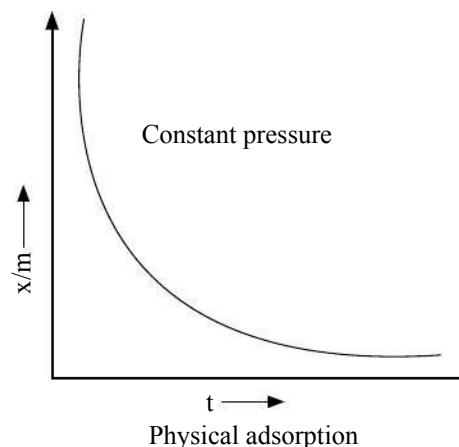
It is reverse of adsorption, i.e., removal of adsorbed substance from the surface of the adsorbent.

## Physical Adsorption



- Here, molecules are attracted to the surface by Weak van der Waal's forces and it is observed at low temperature and on relatively inert surfaces. The forces of attraction are permanent dipole moment in the adsorbed molecules, dispersion effect, polarization and short range repulsive effect.
- It is an instantaneous process and it is a function of coverage surface.
- It is less specific as all gases are adsorbed on metals to some extent.
- It is reversible in nature.
- Adsorption  $\propto$  liquefaction of gases
- It is exothermic in nature so it decreases by the increase of temperature.

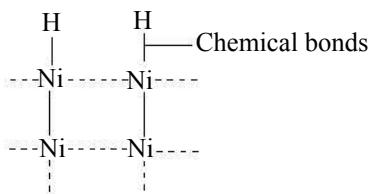
$$\text{Physisorption} \propto \frac{1}{\text{Temperature}}$$



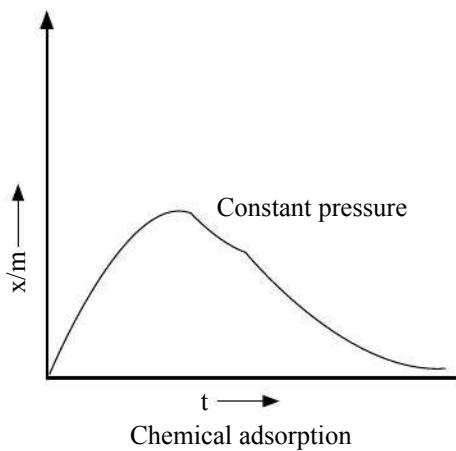
- Here adsorption energy is low and the value is 20-40 kJ/mole
- Here multi-layers are formed.
- Here adsorption  $\propto$  surface area.
- Here, there is no need of activation energy.

Example, Adsorption of nitrogen on mica and gases on charcoal.

## Chemical Adsorption



- Here molecules are held on the surface by strong chemical bonds which may be rapid or slow depending upon the nature of bonding.
- It is very specific in nature.
- It is a function of active sites.
- It is irreversible in nature.
- Gas forming compounds with adsorbent shows it.
- Adsorption energy is high here and the value is 40-400 kJ /mole.
- It is endothermic.
- First it increases with temperature then decreases.



- Here a unimolecular layer is formed.
- Adsorption  $\propto$  surface area
- It needs activation energy.

Example, Adsorption of Oxygen on Tungsten and Hydrogen on Nickel.

## Factors Effecting Adsorption

### 1. Nature of Gas or Adsorbent

It is observed that gases with higher critical temperature or easily liquefiable due to more van der Waal's force of attraction are more adsorbed.

Adsorption  $\propto$  Critical temperature of gas  $\propto$  Liquation of gas

Example,  $\text{NH}_3 > \text{Cl}_2 > \text{HCl} > \text{N}_2 > \text{O}_2 > \text{H}_2$

### 2. Effect of Pressure

At constant temperature, adsorption increases with the increase of pressure

Adsorption  $\propto$  Pressure

### 3. Effect of Temperature

Since it is an exothermic process so it decreases with temperature

Adsorption  $\propto \frac{1}{\text{Temperature}}$

### 4. Surface Area of Adsorbent

Larger the surface area of adsorbent more will be active centers and faster will be the rate of adsorption.

Adsorption  $\propto$  Surface area of a Adsorbent

### 5. Activation of Solid Adsorbent

When adsorbent is sub-divided or already adsorbed gases are removed, it becomes activated adsorbent and rate of adsorption increases.

## Uses

1. Froth floatation method used for concentration of sulphide ores is based on adsorption.
2. Charcoal is used in the production of high vacuum.
3. In the preparation of gas masks using activated charcoal or mixture of adsorbents to avoid poisonous gases like  $\text{CO}$ ,  $\text{CH}_4$  etc.
4. Silica gel, Alumina gel can be used to remove moisture and to control humidity.
5. Animal charcoal removes colour of solution by adsorbing coloured impurities.
6. Coconut charcoal is used to separate mixture of inert gases.
7. In heterogeneous catalysis adsorption of reactants on the solid surface of the catalyst effects rate of reaction.
8. Zeolite ( $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ ) softens water.  

$$\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 + \text{CaCl}_2 \rightarrow \text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{NaCl}$$
  
 Zeolite
9. Adsorption chromatography is used to purify and separate pigments, hormones etc.
10. Lake test used for the detection of  $\text{Al}^{+3}$  is based on adsorption it litmus by the precipitate  $\text{Al(OH)}_3$ .

## REMEMBER

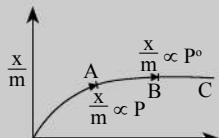
**Adsorption Isotherms:** These are plots between  $x/m$  and  $P$  as follows

1. **Freundlich adsorption isotherm:** According to it

$$\frac{x}{m} \propto P^{1/n}$$

$$\frac{x}{m} = KP^{\frac{1}{n}}$$

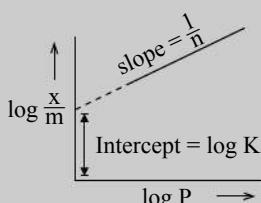
$$\log \frac{x}{m} = \log K + \frac{1}{n} \log P$$



OA: Low pressure

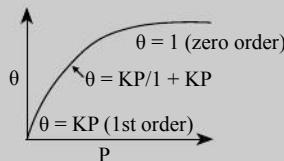
AB: Moderate pressure

BC: High pressure



Here  $\frac{x}{m}$  is the amount of adsorbate adsorbed per gram adsorbent.

2. **Langmuir adsorption isotherm:** According to it



$$\theta = \frac{KP_A}{1 + KP_A} \text{ or } \frac{aP}{1 + bP}$$

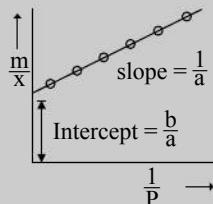
Her a and b are constant.

$\theta$  is covered area

$$\frac{x}{m} = \frac{ap}{1 + bp}$$

$$\frac{x}{m} = \frac{1 + bp}{ap}$$

$$\frac{x}{m} = \frac{1}{ap} + \frac{b}{a}$$



## COLLOIDAL STATE

Thomas Graham (1862) studied the process of diffusion of dissolved substances through a parchment paper or an animal membrane and divided substances into two classes:

- (i) Crystalloids
- (ii) Colloids

- Substances like sugar, urea, common salt, etc., which readily passed through the membrane when in the dissolved state were called crystalloids.
- Substances like starch, glue, gelatin, etc, which in the dissolved state either did not pass at all or passed very slowly through the membrane were called colloids.
- According to the modern view, Colloidal state is an intermediate state between solution and suspension.

## Properties of True Solutions, Colloids and Suspensions

S. No.	Property	True Solution	Colloidal State	Suspension
1.	Nature	Homogeneous	Heterogeneous	Heterogeneous
2.	Particle size	Less than 1 nm i.e., $10^{-7}$ cm or $10 \text{ A}^0$	$1 \text{ to } 100 \text{ nm}$ or $1 \times 10^{-7}$ to $1 \times 10^{-5}$ cm. $10 \text{ to } 1000 \text{ A}^0$	More than 100 nm or more than $1 \times 10^{-5}$ cm or $1000 \text{ A}^0$

S. No.	Property	True Solution	Colloidal State	Suspension
3.	Effect of gravity on particles	No effect, particles do not settle.	No effect, particles do not settle	Particles settle on standing.
4.	Filterability	Pass unchanged through filter paper as well as animal or vegetable membranes	Pass unchanged through filter paper but not through animal or vegetable membranes	Do not pass through filter paper or animal and vegetable membranes
5.	Diffusion	Diffuse rapidly	Diffuse rapidly	Do not diffuse
6.	Visibility	Particles are completely invisible and thus do not scatter light	Particles are invisible to the naked eye, but they scatter light	Particles are visible to naked eye or under a microscope and they scatter light
7.	Appearance of solution	Clear and transparent	Generally clear and transparent	Opaque
8.	Colligative properties	Affect Colligative properties	Do not affect Colligative properties	Do not affect Colligative properties
9.	Tyndall effect	do not exhibit	Exhibits	do not exhibit
10.	Coagulation	They can be coagulated by adding suitable electrolytes	They can be coagulated by adding suitable electrolytes	They are not coagulated

## Dispersion phase and Medium

- A colloid is heterogeneous of two immiscible phases one of which is a continuous phase is

called Dispersion Medium or External phase while the other is a discontinuous phase called Dispersed Phase or Internal phase.

## Types of Colloidal System

Dispersed Phase	Dispersion Medium	Colloidal System	Examples
Gas	Liquid	Foam or froth	Soap sols, lemonade froth, whipped cream
Gas	Solid	Solid foam	Pumice stone, styrene foam, foam rubber, Dried sea foam.
Liquid	Gas	Aerosols of liquids	Fog, clouds, Mist fine insecticide sprays.
Liquid	Liquid	Emulsions	Milk, cold cream, tonics etc.
Liquid	Solid	Gels	Cheese, butter, boot polish, table jellies etc.
Solid	Gas	Aerosols of solids	Smoke, dust, haze
Solid	Liquid	Sols	Paints, starch dispersed in water, gold sol., muddy water, inks etc.
Solid	Solid	Solid sols	Ruby glass, Minerals, gem stones etc.

## Classification of Colloids

Colloids can be classified in a number of ways based upon some of their important characteristics.

### a. Based Upon Appearance

A colloidal system in which the dispersion medium is a liquid or gas is called sol. They are called hydrosols or aquasols if the dispersion medium is water.

- When the dispersion medium is alcohol or benzene, they are accordingly called alcosols or benzsol.
- Colloidal systems in which the dispersion medium is a gas are called aerosols.
- Colloidal systems in which the dispersion medium is a solid are called gels e.g., cheese, etc.

### b. Based Upon Charge

The colloids can be classified into **positive** or **negative** colloids according to the charge present on

the dispersed phase particle forea. Metal hydroxides are generally positively charged while metal sulphides are negatively charged.

### c. Based on Interaction or Affinity of Phase

***Lyophilic Colloids (Suspensoid):*** The colloidal systems in which the particle of dispersed phase have great affinity for the dispersion medium, are called **Lyophilic** (solvent-loving) **Colloids**. Some common examples of lyophilic colloids are gum, gelatin, starch, rubber, protein, etc.

***Lyophobic Colloids (Emulsoid)*** The colloidal systems in which the particles of the dispersed phase have no affinity for the dispersion medium are called **Lyophobic** (solvent hating) **Colloids**. Some examples of lyophobic colloids include sols of metals and their insoluble compounds like sulphides and oxides.

## Difference between Lyophilic and Lyophobic Sols

Property	Lyophilic Sols	Lyophobic Sols
Nature	Reversible	Irreversible
Preparation	They can be prepared very easily by shaking or warming the substance with dispersion medium. They do not require any electrolyte for stabilization.	They can be prepared by special methods and addition of stabilizer is essential for their stability.
Stability	They are very stable and are not easily coagulated by electrolytes.	They are generally unstable and get easily coagulated on addition of electrolytes.
Charge	Particles may carry no charge or very little charge depending upon the pH of the medium	Colloidal particle have characteristic charge (positive or negative).
Viscosity	Viscosity is much higher than that of the medium	Viscosity is nearly the same as that of the medium.
Surface tension	Surface tension is usually less than the medium	Surface tension is nearly the same as that of the medium
Migration in electric field	The particles may or may not migrate in an electric field	The colloidal particles migrate either towards cathode or anode in an electric field
Solvation	Particles are highly solvated	Particles are not solvated

Property	Lyophilic Sols	Lyophobic Sols
Visibility	The particles cannot be seen under ultra microscope.	The particles though invisible, can be seen under ultra microscope.
Tyndall effect	Less distinct	More distinct
Colligative electrolyte	They have relatively higher osmotic pressure, high depression of freezing point and high lowering of vapour pressure.	They have high osmotic pressure, small depression of freezing point, less elevation of boiling point, and less lowering of vapour pressure.
Action of electrolyte	Large amount of electrolyte is required to cause coagulation	Small amount of electrolyte is sufficient to cause coagulation
Conductivity	They show high conductivity which can be measured.	Due to their sensitivity in electrolyte, conductivity can rarely be measured over a considerable range of concentration.
Cataphoresis	The measurement of cataphoresis is difficult.	It can be easily measured.
Examples	Most of the organic substances for Example, starch, gums, proteins, gelatin etc.	Generally inorganic substances Example, metal sols, sulphides and oxides sols.

#### d. Based on Molecular Size

Depending upon the molecular size, the colloidal system has been classified into three classes:

**Multimolecular Colloids** The multimolecular colloidal particles consist of aggregate of atoms or small molecules with diameters less than  $10^{-9}$  m or 1 nm.

For example: gold sol, sulphur sol

**Macromolecular Colloids** The macromolecular colloidal particles themselves are large molecules. They have high molecular weights varying from thousands to millions.

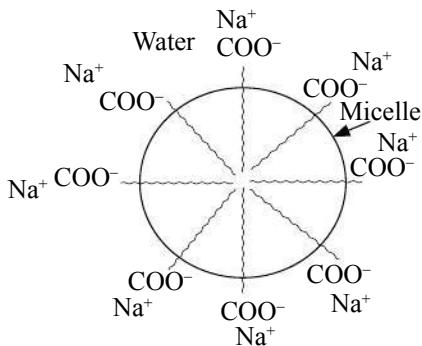
- Naturally occurring macromolecules are such as starch, cellulose and proteins. Artificial macromolecules are such as polyethylene, nylon, polystyrene, dacron, synthetic rubber, plastics etc.

**The Associated Colloids or Micelles** These colloids behave as normal electrolytes at low concentrations but colloids at higher concen-

trations (Critical Micelle concentration that is C.M.C.) because at higher concentrations, they form aggregated (associated) particles called **micelles**. Micelles can be formed above C.M.C. and Kraft temperature for soaps and detergents C.M.C. is  $10^{-4}$  to  $10^{-3}$  M /L. Soap and synthetic detergents are examples of associated colloids. They furnish ions which may have colloidal dimensions



- The long-chain  $\text{RCOO}^-$  ions associate or aggregate at higher concentration and form micelles and behave as colloids. They may contain 100 or more molecules.
- Sodium stearate  $\text{C}_{17}\text{H}_{35}\text{COONa}$  (Anionic Surfactant) is an example of an associated colloid. In water, it gives  $\text{Na}^+$  and stearate,  $(\text{C}_{17}\text{H}_{35}\text{COO})^-$  ions. These ions associate to form micelles of colloidal size.

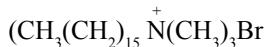


Aggregation of  $\text{RCOO}^-$  ions to form an ionic micelle.

Micelles are spherical but near CMC they are more commonly flattened spheres. At higher concentration, they form extended parallel sheet.

Example: Some cationic surfactants like

- (i) Cetyl trimethyl ammonium bromide



- (ii) P-dodecyl benzene sulphonate.



- (iii) Cetyl Pyridinium chloride.



- (iv) Octodecyl ammonium chloride



## Preparation of Lyophilic Sols

Substances which are termed as intrinsic colloids such as gelatin, rubber, starch etc. are converted into colloidal solutions when warmed with water or some other suitable solvent. The colloidal solutions thus obtained are called lyophilic sols. Such sols are reversible and quite stable. Such substances are converted into colloidal solutions by these two methods

- (a) Dispersion methods
- (b) Condensation methods

## Dispersion Method

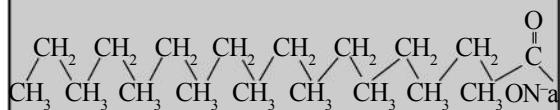
These methods involve the breaking down of bigger particles to the size of colloidal particles. The various dispersion method used are as follows:

- (i) Mechanical dispersion method
- (ii) Electro disintegration method (Bredig's arc method)
- (iii) Peptization

### REMEMBER

#### The Cleansing Action of Soaps

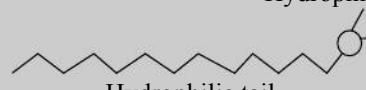
It has been mentioned earlier that a miselle consists of a hydrophobic hydrocarbon like central here. The cleansing action of soap is due to these micelles, because oil and grease can be solubilised their hydrocarbon, like centres which are not otherwise soluble in water. This is shown agrammatically in Fig. 15. The dirt goes out alone with the soap miscelles.



Sodium stearate ( $\text{C}_{17}\text{H}_{35}\text{COO}^-\text{Na}^+$ )

(a)

Hydrophilic head



Hydrophilic tail

(b)

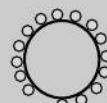


Grease

(c)



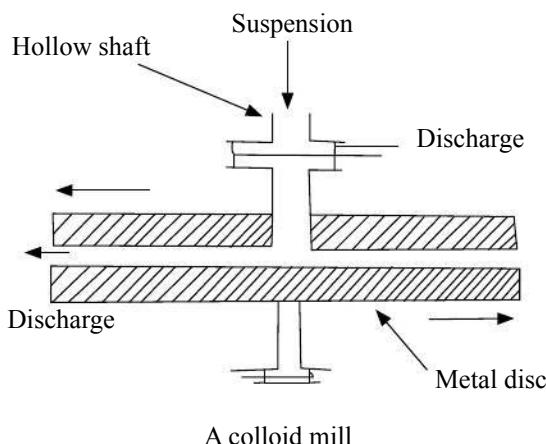
(d)



(e)

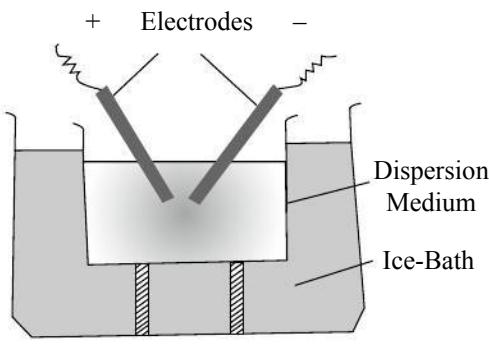
The cleansing action of soap, (a) A sodium stearate molecule (b) The simplified representation of the molecule that show a hydrophilic head and a hydrophobic tail. (c) Grease (oily substance) is not soluble in water (d) When soap is added to water, the non-polar tails of soap molecules dissolve in grease (e) Finally, the grease in the form of miscelles containing grease.

**Mechanical Dispersion Method** The coarse particles of the substance to be dispersed are agitated with dispersion medium, i.e., water or some other liquid to get a suspension. The suspension is then passed through a colloidal mill. Example, colloids of paint, varnish etc.



**Electro-Disintegration Method (Bredig's Arc Method):** Colloidal solutions of metals like gold, Copper, silver, platinum etc. are obtained by electro-disintegration method. (Bredig's arc method).

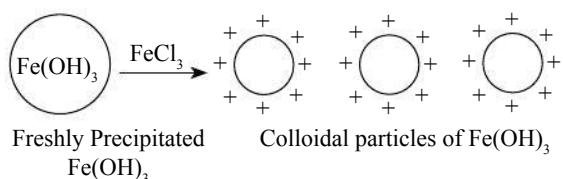
- In this method, the metals (Pt, Ag, Cu) whose colloidal solution is to be prepared are taken as electrodes which are dipped in the cold water having KOH (stabilizer)



Bredig's Arc method

**Peptization** The process which involves the conversion of fresh precipitates into colloidal solution is called peptization and the electrolyte added is called peptizing agent or dispersing agent.

For example, in a freshly precipitated solution of ferric hydroxide when a small amount of electrolyte ferric chloride is added changes into colloid



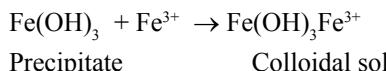
### Example,

- Fresh precipitates of  $\text{CdS}$ ,  $\text{HgS}$  are peptized by  $\text{H}_2\text{S}$ .
- Fresh precipitates of Stannic acid is peptized by  $\text{HCl}_{(\text{aq})}$  or  $\text{NH}_3(\text{e})$

Peptization may be carried out by these methods also:

- Dispersion Medium
- Washing a Precipitate
- Electrolyte

**Cause of Peptization:** On adding the electrolyte to the freshly precipitated substance, the particles of the precipitate preferentially adsorb it a particular type of ions of the electrolyte and get dispersed due to electrostatic repulsion. This produces particles of the colloid. It



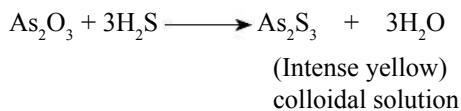
### Condensation Methods

These methods involve the growing of size of the dispersed phase to the size of colloidal particles. The various condensation methods used are

- Chemical methods
- Physical methods

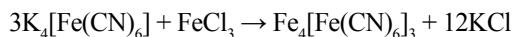
### Chemical Methods

**I. By Double Decomposition:** A colloidal solution of arsenious sulphide is obtained by passing hydrogen sulphide gas through cold dilute solution of arsenious oxide in water as follows.

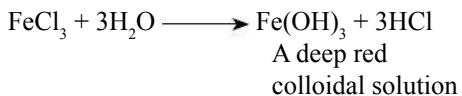


The solution of arsenious sulphide is negatively charged as sulphide ions are absorbed on the solution particles.

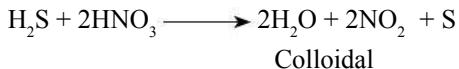
When a dilute solution of  $\text{FeCl}_3$  is mixed with  $\text{K}_4[\text{Fe}(\text{CN})_6]$  a colloidal solution of prussian blue is formed



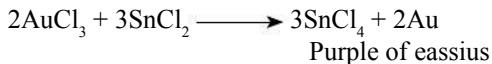
**II. By Hydrolysis:** A deep red colloidal solution of ferric hydroxide is prepared by the hydrolysis of ferric chloride when a dilute solution of it is boiled with water.



**III. By Oxidation:** A colloidal solution of sulphur is obtained by the oxidation of hydrogen sulphide with dilute nitric acid or bromine water or sulphur dioxide.



**IV. By Reduction:** A colloidal solution of gold is obtained by the reduction of gold chloride with stannous chloride or formaldehyde or hydrazine.



### Physical methods

**I. By Exchange of Solvent:** Substances like sulphur, resin, phenolphthalein, etc. Which are highly soluble in alcohol or some other organic solvents yield colloidal solutions when their solutions in alcohol or other solvents are poured into water in which the substances are less soluble. The colloidal solutions thus obtained are less stable.

**II. By Passing the Vapour of Substance into Solvent:** Colloidal solutions of substances like sulphur and mercury in water are prepared by passing the vapours of the substance in cold water containing a little amount of ammonium citrate as a stabilizing agent.

**III. By Excess Cooling:** The colloidal solution of ice in an organic solvent like ether or chloroform is obtained by freezing a solution of water in the solvent.

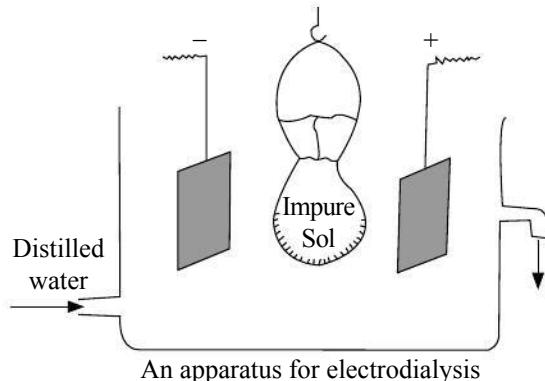
### Purification of Colloidal Solutions

The following methods are commonly used for the purification of a sol.

**(a) Dialysis:** The process of removing a dissolved substance from the colloidal solution (system) by means of diffusion through a suitable

membrane is called dialysis and the apparatus used for this purpose is known as dialyser (Normally, a parchment paper or animal membrane is used ).

**(b) Electrodialysis:** The process of dialysis can be accelerated by applying an electric field. This process is called **Electrodialysis**. In this process, dialysis bag is surrounded by two electrodes. When a high potential is applied, the cation and anion of the electrolyte are attracted by the oppositely charged electrodes and the impurities are easily and quickly removed from the colloidal solution (Sol.). By this method we can not remove impurities of non-electrolytes.



**(c) Ultrafiltration:** This process of separating the colloidal particles from the solvent and solute present by specially prepared filters which are permeable to all substances present except the colloidal particles is called *Ultrafiltration*. For this, we use ultrafilter papers like cellophane membranes.

### Properties of Colloidal Solutions

The various properties of colloidal solutions are: solution of nitro cellulose in a mixture of alcohol and ether).

- (a) Physical properties
- (b) Mechanical properties
- (c) Optical properties
- (d) Electrical properties
- (e) Colligative properties

## Physical Properties

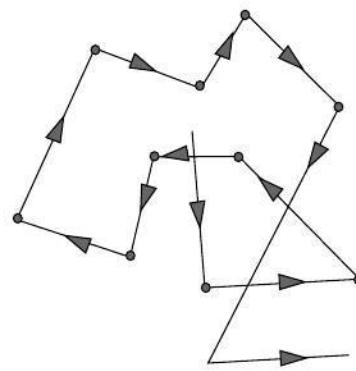
- (i) **Heterogeneity:** Colloidal solutions are heterogeneous in nature consisting of two phases viz., the dispersed phase and the dispersion medium. Experiments like dialysis and ultra filtration indicate the heterogenous nature of the colloidal system.
- (ii) **Filterability:** Colloidal particles can pass through ordinary filter papers as the size of the pores of the filter paper is larger than that of the colloidal particles.
- (iii) **Non-Setting Nature:** Colloidal solutions are quite stable as the colloidal particles remain suspended in the dispersion medium indefinitely i.e., there is no effect of gravity on the colloidal particles.
- (iv) **Colour:** The colour of the colloidal solution is not always the same as the colour of the substances in the bulk. The colour of the colloidal solution depends upon the following factors:
  1. Size and shape of colloidal particles
  2. Wavelength of the source of light
  3. Method of preparation of the colloidal solution
  4. Nature of the colloidal solution
  5. The way an observer receives the light, i.e., whether by reflection or by transmission.
- (v) **Stability:** Colloidal solutions are quite stable.

### Example:

1. Finest gold is red in colour while the size of particles increases, it becomes purple.
2. Dilute milk gives a bluish tinge in reflected light while reddish tinge is transmitted light.

## Mechanical Properties

- (i) **Brownian Movement:** Colloid particles show a ceaseless random and swarming zig-zag motion in dispersal medium known as Brownian movement (shown for the first time by Robert Brown).
- The dispersal medium particles colloid with dispersed phase particles as a result dispersed phase particles move in the direction of net force. This motion increases the stability of colloids.



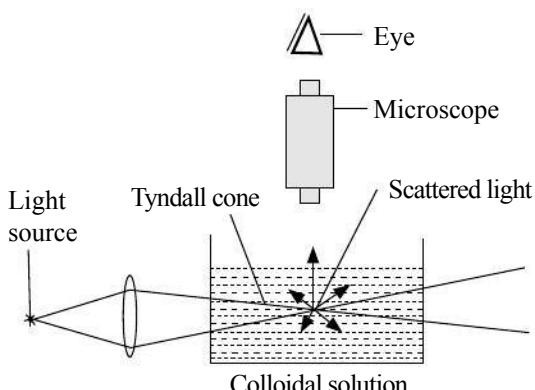
- (ii) **Sedimentation:** The heavier sol particles tend to settle down very slowly under the influence of gravity. It is called sedimentation.
- (iii) **Diffusion:** The colloidal particles have a tendency to diffuse from its high concentration to a low concentration. However the rate of diffusion of colloidal particles is less than that of true solutions.

## Optical Properties (Tyndall Effect)

When a strong and conveying beam of light is passed through a colloidal solution, its path becomes visible (bluish light) when viewed at right angles to the beam of light.

The Tyndall effect was used by **Zsigmondy** and **Siedentopf** in devising ultramicroscope.

- It is due to scattering of light by colloid particles Example, Sky looks blue, dust particles can be seen in the light coming from ventilator in a dark room, tail of comet etc.



**Conditions needed for Tyndall effect**

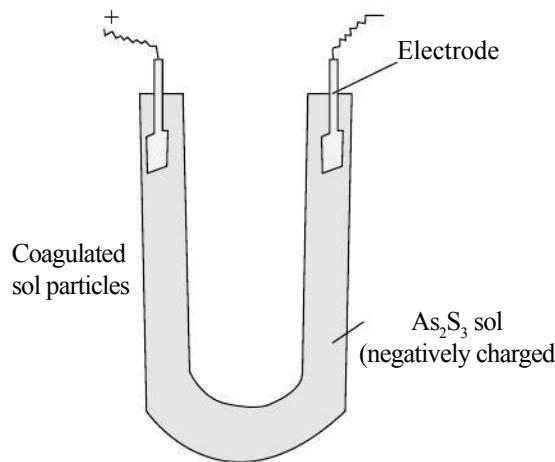
It is observed only when:

- (1) The diameter of the dispersed particles is not much smaller than the wave length of the light used.
- (2) The refractive indices of the dispersed phase and the dispersion medium must differ largely in magnitude.

**Electrical Properties**

The two electrical properties of colloidal solutions are

**(i) Electrophoresis or Cataphoresis:** It is the phenomenon involving the migration of colloidal particles under the influence of electric field towards the oppositely charged electrode is known as electrophoresis or cataphoresis. It is useful in deciding charge present on colloid particles.



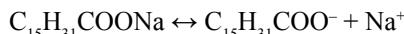
**(ii) Electro-Osmosis:** It involves the migration of the dispersion medium and not the colloidal particles under influence of an electric field. It is useful in removal of water from peat in drying dye in dewatering moist clay.

**Origin of Charge**

Various reasons have been given regarding the origin of charge on the colloidal particles. These are as follows:

**I. Frictional Electrification:** It is believed to be frictional due to the rubbing of the dispersed phase particles with medium molecules.

**II. Dissociation of the Surface Molecules:** It leads to electric charge on colloidal particles. For example, an aqueous solution of soap (sodium palmitate) dissociates into ions.



Sod. palmitate

- The  $\text{Na}^+$  ions pass into the solution while  $\text{C}_{15}\text{H}_{31}\text{COO}^-$  ions have a tendency to form aggregates due to weak attractive forces present in the hydrocarbon chains. Thus, the anions which are of collidal size bear negative charge.

**III. Preferential Adsorption of Ions From Solution:** The charge on the colloidal particles is generally acquired by preferentially adsorbing positive or negative ions from the electrolyte.

- $\text{AgCl}$  particles can absorb  $\text{Cl}^-$  ions from chloride solutions and  $\text{Ag}^+$  ions from solution having  $\text{Ag}^+$  ions; the solution will be negatively charged in the first case and positively charged in the second case.  $\text{Ag I}$  particles adsorb  $\text{Ag}^+$  ions from the solution of  $\text{AgNO}_3$  and  $\text{I}^-$  from  $\text{KI}$  solution  $\text{As}_2\text{S}_3$  adsorb  $\text{S}^{2-}$  from  $\text{H}_2\text{S}$  Solution so they are negatively charged.

**Electrical Charged Sols.**

- Positively charged sols: Example: Ferric hydroxide, aluminium hydroxide, basic dyes such as methylene blue, Hemoglobin protein in acidic medium  $\text{TiO}_2$  etc.
- Negatively charged sols: Metals, such as Pt, Au, Ag, Metal sulphides. Example, arsenius sulphide, gum, starch, clay, salicylic acid, acid dyes (such as eosin).

**Colligative Properties**

Colloidal solutions too exhibit Colligative properties such as osmotic pressure, lowering of vapour pressure, depression in freezing point and elevation in boiling point.

- The effect of colloidal particle on Colligative properties except osmotic pressure is very small due to the large size of colloidal particles.

**Coagulation of Flocculation**

The colloidal sols are stable due to the presence of electric charges on the colloidal particles. Because

of the electrical repulsion, the particles do not come close to one another to form precipitates.

- The removal of charge by any means will lead to the aggregation of particles for precipitation is known as coagulation and the minimum amount of an electrolyte required to cause precipitation of one liter of a colloidal solution is called coagulation value or flocculation value of the electrolyte for the sol.
- The reciprocal of coagulation value is regarded as the coagulating power.

### Hardy-Schylz Rules

According to it, "Higher the valency of the active electrolyte ion, the more is its power to precipitate the sol"

- The coagulation power of cations for negatively charged colloids is  $\text{Si}^{4+} > \text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+$ .
- The coagulation power of anion for positively charged sol is  $[\text{Fe}(\text{CN})_6]^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$ .

### Protection and Gold Number

Protection involves the protection of lyophobic colloid from Coagulation by using a lyophilic colloid which is called protective colloid and the protection power of lyophilic colloids can be expressed in terms of Gold number which is explained as

Gold number is the number of milligrams of the protective colloid needed to prevent the coagulation of a standard 10 ml gold sol when 1 ml of 10% solution of sodium chloride is added to it.

- Smaller the gold number greater will be the protection power.

### Example:

- (i) Gelatin is added in the preparation of icecream to protect colloid particles rice from being coagulated.
- (ii) Protargols and argyrols are used in eye drops.

Protective colloid	Gelatin	Hemo-globin	Gum Arabic	Egg Albumin	starch
Gold Number	0.005	0.03	0.15	0.08	25
	-0.01				

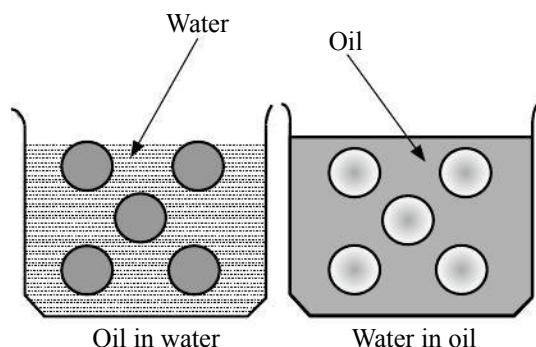
## EMULSIONS

The colloidal solution of two immiscible liquids in which the liquid acts as the dispersed phase as well as the dispersion medium. There are two types of emulsions i.e., (i) oil in water (ii) water in oil emulsions.

To test the type of emulsion either dye test or conductance measurement test may be performed.

*Hydrophilic Emulsifiers* dissolve better in water than in oil and hence these promote formation of O/W emulsions. Example, milk.

*Hydrophobic Emulsifiers* on the other hand dissolve better in oil than in water and hence these favour formation of W/O emulsions. Example, cold cream.



Types of Emulsions.

### Uses of Emulsions

- (i) Many pharmaceutical preparations medicines, ointments, creams and various lotions are emulsions. It is believed that medicines are more effective and easily assimilated by the body tissues when they are in colloidal form i.e., emulsion.
- (ii) All paints are emulsions.
- (iii) The digestion of fat in the intestines is helped by emulsification. A little of the fat forms a medium soap (emulsifier) with the alkaline solution of the intestine and this soap emulsifies the rest of the fats thus making it easier for the digestive enzymes to do their metabolic functions.
- (iv) Soaps and detergents remove dust and dirt from the dirty piece of cloth by making oil in water emulsion.
- (v) Milk is an emulsion of liquid fats droplets in water.

- (vi) In froth floatation process, an oil is added to the finely-divided ore taken in water. The particles of ore go on to the surface due to the formation of foams while the other impurities are left at the bottom of the vessel.
- (vii) The emulsion of asphalt in water is used in road-making and building.

## GELS

Here, the dispersed phase is of liquid while dispersion medium is that of liquid.

- Sols when coagulated under some special conditions, change into semi-rigid mass, enclosing whole amount of liquid within itself. This semi-rigid mass is known as gel.
- Hydrophilic sols of gelatin, agar-agar, gum-arabic, mastic and gamboge etc., can be converted into gels by cooling them under moderate concentration condition.
- The hydrophobic gels like silicic acid, aluminium hydroxide, commonly known as silica gel and alumina gel, are prepared by double decomposition method.
- Change of solvent method is also used to prepare hydrophobic gels. For example when ethanol is added rapidly to the solution of calcium acetate of fair concentration gelation takes place after sometime.

### Elastic Gels

These are reversible gels. When partially dehydrated, they change into solid mass which, however, changes back into original form on simple addition of water followed by slightly heating it required.

- Elastic gels can imbibe water when placed in it and undergo swelling. This is known as imbibition or swelling.

Example, Gelatin, agar-agar and starch.

### Non-Elastic Gels

These are irreversible gels, when hydrated, they become glassy or change into powder which on

hydration followed by warming do not change back to original gel.

- Non-elastic gels cannot imbibe water or they do not undergo swelling phenomenon.
- Silica, alumina, and ferric oxide gels are important examples of non-elastic gels.
- Both elastic and non elastic gels undergo shrinking in volume when allowed to stand. This phenomenon is known as syneresis. The application of external pressure to gel increases the process of syneresis.

### Thixotropy

Some of the gels, specially gelatin (reversible) and silica (irreversible) liquefy on shaking changing into corresponding sols. The sol on standing reverts back to gel. This sol-gel transformation is known as thixotropy.

### Enhance Your Knowledge

- (i) The colloidal sol of cellulose nitrate prepared in ethanol is known as collodion.
- (ii) The process of dialysis finds use in the purification of blood by artificial kidney.
- (iii) The blue colour of sky is due to scattering of light by colloidal dust particles dispersed in air.
- (iv) When a negatively charged  $\text{As}_2\text{S}_3$  sol is added to positively charged  $\text{Fe(OH)}_3$  sol in suitable amounts, both the sols are precipitated simultaneously. This is termed as mutual coagulation.
- (v) Flocculation value of an ion  

$$\propto \frac{1}{\text{coagulating power of the ion}}$$
- (vi) Zsigmondy was awarded the 1925 chemistry Nobel Prize for this contribution to colloidal chemistry.
- (vii) Ostwald introduced Congo Rubin Number which is defined as “The amount of protective colloid in that prevents colour change in 100 ml milligram of 0.01% Congo Rubin dye from the addition of 0.16 gm equivalence (0.5 Kcl)

## Solved Problems from the IITs

1. 1g of charcoal adsorbs 100ml of 0.5 M  $\text{CH}_3\text{COOH}$  to form a mono layer, and thereby the molarity of  $\text{CH}_3\text{COOH}$  reduces to 0.49M. Calculate the surface area of the Charcoal adsorbed by each molecule of acetic acid. Surface area of Charcoal =  $3.01 \times 10^2 \text{ m}^2/\text{g}$ , [IIT 2003]

**Solution** 100 ml of 10.5 M  $\text{CH}_3\text{COOH}$  contains  $\text{CH}_3\text{COOH} = 0.05$  mole. After adsorption,  $\text{CH}_3\text{COOH}$  Present = 0.049 mole. Acetic acid adsorbed by 1g Charcoal = 0.001 mole =  $6.02 \times 10^{20}$  molecules

$$\text{Surface area of 1g of Charcoal} = 3.01 \times 10^2 \text{ m}^2$$

Surface area of 1g of Charcoal adsorbed by each molecule

$$= \frac{3.01 \times 10^2}{6.02 \times 10^{20}} = 5 \times 10^{-19} \text{ m}^2$$

2. 20% of surface sites are occupied by  $\text{N}_2$  molecules. The density of surface sites is  $6.023 \times 10^{14} \text{ cm}^{-2}$  and total surface area is 1000  $\text{cm}^2$ . The catalyst is heated to 300k while  $\text{N}_2$  is complete by desorbed into a pressure of 0.001 atm. and volume 2.46  $\text{cm}^3$ . Find the active sites occupied by each  $\text{N}_2$  molecule.

**Solution** Step I:- It can be find out in these steps density of surface sites =  $6.023 \times 10^{14} \text{ cm}^{-2}$  Total surface sites =  $1000 \text{ cm}^2 = 10^3 \text{ cm}^2$

Hence total no. of surface sites

$$= (6.023 \times 10^{14}) \times (10^3) = 6.023 \times 10^{17}$$

Step II:- Calculation of surface sites occupied by  $\text{N}_2$  molecules surface sites occupied

$$= \frac{20}{100} \times 6.023 \times 10^{17} = 1.2046 \times 10^{17}$$

Step III:- Calculation of total no. of  $\text{N}_2$  molecules

$$P = 0.001 \text{ atm}$$

$$v = 2.40 \text{ cm}^3 = 2.46 \times 10^{-3} \text{ l}$$

$$T = 300\text{K}$$

$$Pv = nRT \text{ or } n$$

$$= \frac{10^{-3} \times 2.46 \times 10^{-3} \times 2}{0.0821 \text{ Latm K}^{-1} \text{ mol}^{-1} \times 300\text{K}}$$

$$= 10^{-7} \text{ mole}$$

Hence no. of molecule

$$= (10^{-7}) \times (6.023 \times 10^{23})$$

$$= 60.23 \times 10^{16}$$

## MULTIPLE-CHOICE QUESTIONS

### Straight Objective Type Questions (Single Choice only)

1. Which one of the following method is commonly used method for destruction of colloid?
  - Condensation
  - Dialysis
  - By adding electrolyte
  - Filtration by animal membrane
2. The movement of colloidal particles towards the oppositely charged electrodes on passing electric current is known as
  - Tyndall effect
  - cataphoresis
  - Brownian movement
  - none of these
3. Which one of the following reactions is an example of heterogeneous catalysis?
  - $2\text{CO} + \text{O}_2 \xrightarrow{\text{NgO}} 2\text{CO}_2$   
g g g
  - $2\text{SO}_2 + \text{O}_2 \xrightarrow{\text{NOg}} 2\text{SO}_3$   
g g g
  - $2\text{CO} + \text{O}_2 \xrightarrow{\text{Pt(s)}} 2\text{CO}_2$   
g g g
  - $\text{CH}_3\text{CHO} \xrightarrow[\text{g}]{\text{I}_2} \text{CH}_4 + \text{CO}$   
g g g
4. Which of the following is readily absorbed by activated metals?
 

a. O <sub>2</sub>	b. N <sub>2</sub>
c. CO <sub>2</sub>	d. CO
5. Which of the following is adsorbed in maximum amount by activated charcoal?
 

a. N <sub>2</sub>	b. CO
c. HCl	d. CO <sub>2</sub>
6. Cod liver in an example of
  - oil emulsion
  - oil in water emulsion
  - water in oil emulsion
  - water in water emulsion

7. The ability of a catalyst to accelerate the chemical reaction is known as
  - selectivity
  - activity
  - positive catalysis
  - negative catalysis
8. The solution of rubber is an example of
  - lyophonic colloid
  - multimolecular colloid
  - associated colloid
  - macromolecular colloid
9. The reactions in zeolite catalysts depend upon
 

a. apertures	b. size of cavities
c. pores	d. all of these
10. The amount of gas adsorbed physically on charcoal
  - increases with pressure and decreases with temperature
  - increases with temperature and decreases with pressure
  - increases with temperature and pressure
  - increases either temperature or pressure.
11. Smoke is a colloidal dispersion of a
 

a. solid in a gas	b. liquid in a gas
c. gas in a solid	d. gas in a gas
12. Which of the following is used for the destruction of colloids?
 

a. ultrafiltration	b. adding electrolyte
c. both (a) and (b)	d. dialysis
13. Colloidal solution of silver is prepared by
 

a. Bredig's arc method
b. peptization
c. colloidal milk
d. double decomposition method
14. In which of the following, Tyndall effect is not observed?
 

a. gold sol	b. sugar solution
c. emulsions	d. suspension

15. Which of the following ions have minimum flocculation value?
- $\text{PO}_4^{3-}$
  - $\text{SO}_4^{2-}$
  - $[\text{Fe}(\text{CN})_6]^{4-}$
  - $\text{Cl}^-$
16. Which of the following colloidal solution is commonly used as germ killer?
- colloidal sulphur
  - colloidal gold
  - colloidal silver
  - colloidal antimony
17. A biological catalyst is essentially
- a carbohydrate
  - an enzyme
  - a nitrogen molecules
  - an amino acid
18. In homogeneous catalytic reactions, the rate of reaction
- depends upon the concentration of catalyst
  - depends upon physical state of catalyst
  - is independent of the physical state of catalyst
  - is independent of the concentration of catalyst
19. The process of separating of cream from milk is called
- emulsification
  - demulsification
  - emulsions
  - electro osmosis
20. The adsorption of solids, from a solution is called
- chemical adsorption
  - physical adsorption
  - positive adsorption
  - negative adsorption
21. Alum is widely used to purify water since
- it forms complex with clay particles
  - it coagulates the mud particles
  - it exchanges  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions present in hard water
  - its sulphate ion is water purifier.
22. Which of the following has maximum flocculation value for a negatively charge sol?
- $\text{BaCl}_2$
  - $\text{NaCl}$
  - $\text{AlCl}_3$
  - $\text{MgCl}_2$
23. When a few typical solutes are separated by a particular selective membrane, such as protein particles from blood corpuscles, the process is called
- exosmosis
  - dialysis
  - transpiration
  - endosmosis
24. The bleeding on a wound is stopped by the application of ferric chloride due to
- blood starts flowing in the opposite direction
  - ferric chloride seals the blood vessels
  - blood reacts and a solid is formed which seals the blood vessels
  - blood is coagulated and the blood vessels are sealed.
25. Which of the following colloidal solution is used in photography?
- colloidal silver bromide
  - colloidal gold
  - colloidal silver
  - colloidal sulphur
26. Which of the following kinds of catalysis can be explained by the adsorption theory?
- enzyme catalysis
  - homogeneous catalysis
  - acid base catalysis
  - heterogeneous catalysis
27. Position of non-polar and polar part in micelles:
- polar at outer surface but non polar at inner surface
  - polar at inner surface non polar at outer surface
  - distributed over all the surface
  - are present in the surface only
28. Which one of the following is correctly matched?
- Solid sol-cake
  - Aerosol-Smoke
  - Foam-mist
  - Emulsion-Curd
29. Surface tension of lyophilic sols is
- Equal to that of  $\text{H}_2\text{O}$
  - Lower than that of  $\text{H}_2\text{O}$
  - More than that of  $\text{H}_2\text{O}$
  - None of these
30. Which of the following is correct according to Freundlich adsorption isotherm?
- $X/m \propto P^0$
  - $X/m \propto P^n$
  - $X/m \propto 1/P$
  - $X/m \propto P^{1/n}$

**10.18 ■ Surface Chemistry**

- b. sodium acetate  
c. urea  
d. cetyltrimethyl ammonium bromide
- 46.** Eosin used to detect the end point of precipitation titration by adsorption is called  
 a. absorption indicator  
 b. adsorption indicator  
 c. normal indicator  
 d. chemical indicator
- 47.** Colloidal solutions are not purified by  
 a. electrodialysis      b. electrophoresis  
 c. ultrafiltration      d. dialysis
- 48.** Medicines are more effective, if they are used in  
 a. solution state      b. gaseous state  
 c. colloidal state      d. solid state
- 49.** Artificial rain is caused by spraying  
 a. neutral charged colloidal dust over a cloud  
 b. same charged colloidal dust over a cloud  
 c. Both (a) and (b)  
 d. opposite charged colloidal dust over a cloud
- 50.** Which of the following process is responsible for the digestion of fats in the intestines?  
 a. electro osmosis  
 b. demulsification  
 c. electrophoresis  
 d. emulsification
- 51.** Which of the following is an example of homogeneous catalysis?  
 a. oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  in the contact process  
 b. manufacture of  $\text{NH}_3$  by Heber's process  
 c. oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  in the lead chamber process  
 d. oxidation of  $\text{NH}_3$  to NO in Ostwald's process
- 52.** Which of the following is an example of heterogeneous catalyst?  
 a.  $2\text{SO}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4$   
 b.  $2\text{H}_2\text{O}_2(\text{l}) + \text{MnO}_2(\text{s}) \rightarrow 2\text{H}_2\text{O} + \text{O}_2$   
 c.  $2\text{H}_2\text{O}_2(\text{aq}) \xrightarrow{\text{FeCl}_3} 2\text{H}_2\text{O} + \text{O}_2$   
 d. sucrose +  $\text{H}_2\text{O} \xrightarrow{\text{H}^+}$  glucose + fructose
- 53.** Which of the following is used as a catalyst for preparing Grignard reagent?  
 a. manganese dioxide  
 b. iron powder  
 c. activated charcoal  
 d. dry ether
- 54.** Which of the following is a lyophilic colloidal solution?  
 a. aqueous starch solution  
 b. aqueous protein solution  
 c. gold sol  
 d. polymer solutions in some organic solvents
- 55.** Bredig's arc method can not be used to prepare colloidal solution of which of the following?  
 a. Ag                          b. Fe  
 c. Pt                          d. Au
- 56.** Potassium stearate is obtained by the saponification of an oil or fat. It has the formula  $\text{CH}_3 - (\text{CH}_2)_{16} - \text{COO}^- \text{K}^+$ . The molecule has a lyophobic end ( $\text{CH}_3$ ) and a lyophilic and  $\text{COO}^- \text{K}^+$ . Potassium stearate is an example for  
 a. lyophobic colloid  
 b. lyophilic colloid  
 c. multimolecular colloid  
 d. associated colloid or micelle
- 57.** Which one of the following forms micelles in aqueous solution above certain concentration?  
 a. dodecyl trimethyl ammonium chloride  
 b. glucose  
 c. urea  
 d. pyridinium chloride
- 58.** The efficiency of an enzyme to catalyse a reaction is due to its capacity to  
 a. reduce the activation energy of the reaction  
 b. form strong enzyme substrate complex  
 c. decrease the bond energy of all substrate molecules  
 d. increase the free energy of the catalyst substrate reaction
- 59.** What is the equation form of Langmuir isotherm under high pressure?  
 a.  $x/m = a/b$                           b.  $x/m = a.p$   
 c.  $x/m = 1/a.p$                           d.  $x/m = b/a$
- 60.** An example of autocatalysis is  
 a. Decomposition of  $\text{KClO}_3$  to  $\text{KCl}$  and  $\text{O}_2$   
 b. Oxidation of oxalic acid by acidified  $\text{KMnO}_4$

## 10.20 ■ Surface Chemistry

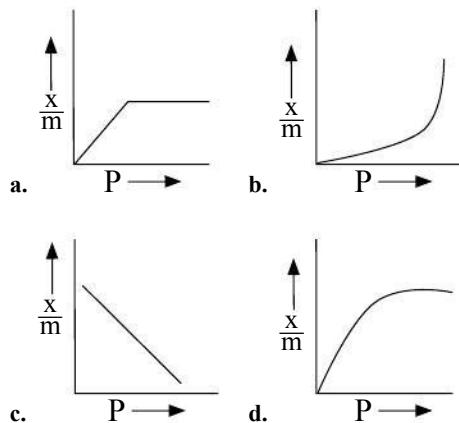
- c. Oxidation of NO to  $\text{NO}_2$   
d. Oxidation of  $\text{SO}_2$  to  $\text{SO}_3$
61. The Langmuir adsorption isotherm is deduced using the assumption:  
a. The adsorption takes place in multi layers  
b. The adsorption sites are equivalent in their ability to adsorb the particles.  
c. The heat of adsorption varies with coverage.  
d. The adsorbed molecules interact with each other.
62. Which one of the following is a homogeneous catalysis?  
a. Synthesis of ammonia by Haber's process  
b. Hydrogenation of oils  
c. Manufacture of sulphuric acid by contact process  
d. Manufacture of sulphuric acid by lead chamber process
63. The physical states of dispersing phase and dispersion medium in colloid like pesticides spray respectively are  
a. Liquid, solid      b. Liquid, gas  
c. Gas, liquid      d. Solid, gas
64. The continuous phase contains the dispersed phase throughout. An example for this is  
a. Water in milk  
b. Fat in milk  
c. Water droplets in mist  
d. Oil in water
65. Alum is widely used to purify water since  
a. it forms complex with clay particles  
b. it coagulates the mud particles  
c. it exchanges  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions present in hard water  
d. Its sulphate ion is water purifier.
66. The basic principle of Cottrell's precipitator is  
a. Neutralization of charge on colloidal particles  
b. Peptization  
c. Scattering of light  
d. Le-Chatelier principle
67. On addition of one ml of solution of 10% NaCl to 10 ml of red sol in presence of 0.025 g of starch, the coagulation is just prevented. The gold number of starch is  
a. 0.25      b. 0.025  
c. 2.5      d. 25
68. Lyophilic sols are more stable than lyophobic sols because the particles  
a. are positively charged  
b. are negatively charged  
c. are solvated  
d. repel each other  
e. are heavy
69. In chemisorption, adsorption decreases after increase due to  
a. endothermic nature of adsorption  
b. exothermic nature of absorption  
c. exothermic nature of adsorption  
d. weak force of van der Waal's
70. In the reaction  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \text{(s)} + \text{H}_2\text{O} \text{(l)} \xrightarrow{\text{dilute H}_2\text{SO}_4} \text{C}_6\text{H}_{12}\text{O}_6 \text{(aq)} + \text{C}_6\text{H}_{12}\text{O}_6 \text{(aq)}$ , dilute  $\text{H}_2\text{SO}_4$  acts as  
a. homogeneous catalyst  
b. heterogeneous catalyst  
c. heterogeneous reactant  
d. homogeneous reactant
71. Rate of adsorption of gas is greater when pressure  
a. For low range of pressure  
b. For every range of pressure  
c. For moderate range of pressure  
d. For high range of pressure
72. Which acts as auto-catalyst during titration of  $\text{KMnO}_4$  and oxalic acid in presence of  $\text{H}_2\text{SO}_4$ ?  
a.  $\text{H}_2\text{SO}_4$       b.  $\text{KMnO}_4$   
c. oxalic acid      d.  $\text{MnSO}_4$
73. Which are the applications of adsorption?  
(i) Chromatographic analysis  
(ii) In gas mask  
(iii) Artificial rain  
(iv) To create vacuum  
a. (i), (ii)      b. (ii), (iv)  
c. (i), (iii), (iv)      d. (ii), (iii), (iv)
74. The size of particles in suspension, true solution and colloidal solution varies in the order:  
a. suspension > colloidal > true solution  
b. true solution > suspension > colloidal  
c. suspension > colloidal = true solution  
d. suspension = colloid < true solution

75. Activated charcoal can be obtained by
- heated charcoal with steam so that it becomes more porous
  - reacted with conc. $\text{HNO}_3$
  - adding  $\text{Ca}_3(\text{PO}_4)_2$  to charcoal
  - adding impurity to charcoal

### Brainteasers Objective Type Questions (Single choice only)

76. The volume of a colloidal particle,  $V_c$  as compared to the volume of a solute particle in a true solution  $V_s$  could be
- $\sim 1$
  - $\sim 10^{23}$
  - $\sim 10^{-3}$
  - $\sim 10^3$
77. If  $(x/m)$  is the mass of adsorbate adsorbed per unit mass of adsorbent,  $p$  is the pressure of the adsorbate gas and  $a$  and  $b$  are constants, which of the following represents "Langmuir adsorption isotherm"?
- $\log(x/m) = \log(a/b) + (1/a)\log p$
  - $x/m = b/a + 1/ap$
  - $x/m = 1 + bp/ap$
  - $1/(x/m) = b/a + 1/ap$
78. The catalyst used in Zeigler process for polyethylene manufacture
- consists of aluminium triethyl and titanium tetrachloride
  - is vanadium pentoxide
  - consists of aluminium chloride and titanium dioxide
  - is finely divided nickel
79. In coagulating the colloidal solution of  $\text{As}_2\text{S}_3$ , which has the minimum coagulating value?
- $\text{KCl}$
  - $\text{NaCl}$
  - $\text{AlCl}_3$
  - $\text{BaCl}_2$
80. When a graph is plotted between  $\log x/m$  and  $\log p$ , it is straight line with an angle  $45^\circ$  and intercept 0.3010 on y-axis. If initial pressure is 0.4 atm, what will be the amount of gas adsorbed per gm of adsorbent?
- 0.2
  - 0.6
  - 0.4
  - 0.8
81. The diameter of colloidal particle ranges from
- $10^{-9} \text{ m to } 10^{-6} \text{ m}$
  - $10^{-6} \text{ m to } 10^{-3} \text{ m}$

- c.  $10^{-12} \text{ m to } 10^{-9} \text{ m}$
- d.  $10^{-3} \text{ m to } 10^{-6} \text{ m}$
82. Which of the following colloidal solution is prepared when very dilute solution of ferric chloride reacts with potassium ferrocyanide?
- Prussian blue
  - arsenic sulphide
  - ferric hydroxide
  - extrinsic colloid
83. Which of the following graphs represents adsorption (where  $x$  = amount of gas taken,  $m$  = mass of solid,  $p$  = gas pressure)?



84. What is the correct sequence of the increasing effectiveness of the following electrolyte for the coagulation of ferric hydroxide sol?
- $\text{K}_4[\text{Fe}(\text{CN})_6]$
  - $\text{FePO}_4$
  - $\text{BaSO}_4$
  - $\text{SnCl}_4$
- Select the correct answer using the codes given below:
- 4, 2, 1, 3
  - 4, 3, 2, 1
  - 1, 2, 3, 4
  - 3, 4, 2, 1
85. Which one of the following acts as the best coagulating agents for ferric hydroxide sol?
- Potassium ferricyanide
  - Aluminium chloride
  - Magnesium chloride
  - Hydrochloric acid
  - Potassium oxalate
86. If a freshly prepared ppt. of  $\text{SnO}_2$  is peptized by a small amount of  $\text{NaOH}$ , the colloidal particles can be represented as
- $[\text{SnO}_2]\text{Sn}^{+4} \quad \text{OH}^-$
  - $[\text{SnO}_2]\text{Sn}^{+4} \quad \text{O}^{-2}$

**10.22** ■ Surface Chemistry

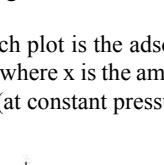
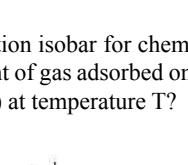
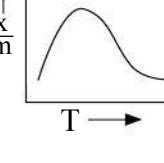
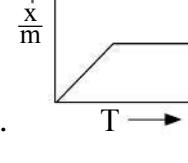
- c.  $[\text{SnO}_2]\text{Na}^+$       OH<sup>-</sup>  
d.  $[\text{SnO}_2]\text{SnO}_3^{+2}$       2Na<sup>+</sup>

87. On adding one ml of solution of 10% NaCl to 10 ml of gold sol in the presence of 0.25 g of starch, the coagulation is just prevented. The gold number of starch is  
a. 25      b. 50  
c. 150      d. 250  
e. 2.50

88. 2.5 g of a protective colloid is required to prevent coagulation of 100 cc gold sol when 10 cc of 10 % NaCl solution is added. The gold number of protective colloid is  
a. 250      b. 125  
c. 2.50      d. 525

89. The adsorption of a gas, on a solid surface, varies with pressure of the gas in which of the following manner?  
a. slow → fast → independent of the pressure  
b. fast → slow → independent of the pressure  
c. independent of the pressure → slow → fast  
d. independent of the pressure → fast → slow

90. Plot of log x/m against log P is a straight line inclined at an angle of 45°. When the pressure is 0.5 atm and Freundlich parameter, K is 10, the amount of solute adsorbed per gram of adsorbent will be (log 5 = 0.6990)  
a. 1g      b. 0.5 g  
c. 3.6 g      d. 5 g  
e. 2 g

91. Which plot is the adsorption isobar for chemisorption where x is the amount of gas adsorbed on mass 'm' (at constant pressure) at temperature T?  
a.  b.   
c.  d. 

92. A plot of log x/m versus log P for the adsorption of a gas on a solid gives a straight line with slope equal to  
a. 1/n      b. log K  
c. - log K      d. n

93. Potassium stearate is obtained by the saponification of an oil or fat. It has the formula CH<sub>3</sub>-(CH<sub>2</sub>)<sub>16</sub>-COO<sup>-</sup>K<sup>+</sup>. The molecule has a lyophobic end (CH<sub>3</sub>) and a lyophilic end COO<sup>-</sup>K<sup>+</sup>. Potassium stearate is an example for  
(1) lyophobic colloid  
(2) associated colloid or micelle  
(3) multimolecular colloid  
(4) macromolecular colloid  
a. 2 only      (B) 1 and 2  
c. 3 and 4      (D) 4 only

94. In the stoichiometry of natural fauzasite- a zeolite with formula Na<sub>x</sub>[(AlO<sub>2</sub>)<sub>56</sub>(SiO<sub>2</sub>)<sub>136</sub>]. 250 H<sub>2</sub>O, the value of x is  
a. 154      b. 36  
c. 46      d. 56

95. At STP the volume of nitrogen gas required to cover a sample of silica gel, assuming Langmuir monolayer adsorption, is found to be 1.33 cm<sup>3</sup> g<sup>-1</sup> of the gel. The area occupied by a nitrogen molecule is 0.15 nm<sup>2</sup>. What is the surface area per gram of silica gel?  
a. 5.568 m<sup>2</sup> g<sup>-1</sup>      b. 1.5 m<sup>2</sup> g<sup>-1</sup>  
c. 5.343 m<sup>2</sup> g<sup>-1</sup>      d. 1.33 m<sup>2</sup> g<sup>-1</sup>

96. Which of the following electrolyte will have maximum flocculation value for Fe(OH)<sub>3</sub> sol?  
a. (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>      b. K<sub>2</sub>SO<sub>4</sub>  
c. NaCl      d. Na<sub>2</sub>S

97. Gold numbers of protective colloids A, B, C and D are 0.50, 0.01, 0.10 and 0.005, respectively. The correct order of their protective powers is  
a. D < A < C < B  
b. C < B < D < A  
c. A < C < B < D  
d. B < D < A < C

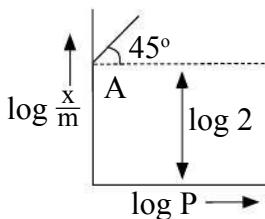
98. The number of moles of lead nitrate needed to coagulate 2 mol of colloidal [AgI] I<sup>-</sup> is

- a. 2                    b. 1  
c. 1/3                d. 2/4 4/1

99. Which methods of preparation of sol involve chemical reaction?

- (i) Exchange of solvent
  - (ii) Hydrolysis
  - (iii) Mechanical dispersion
  - (iv) Double decomposition
- a. (ii), (iv)              b. (iv)  
c. (ii)                    d. (ii), (iii), (iv)

100. Graph between  $\log \frac{x}{m}$  and  $\log P$  is a straight line at angle  $45^\circ$  with intercept OA as shown.



Hence,  $\frac{x}{m}$  at a pressure of 2 atm is:

- a. 4                    b. 2  
c. 1                    d. 8

101. For the coagulation of 100 ml of arsenious sulphide solution, 5 ml of 1 M NaCl is required. What is the coagulation value of NaCl?

- a. 50                    b. 40  
c. 75                    d. 25

102. The volume of gases  $H_2$ ,  $CH_4$ ,  $CO_2$  and  $NH_3$  adsorbed by 1 g of charcoal at 288 K are in the order of

- a.  $CO_2 > NH_3 > H_2 > CH_4$   
b.  $NH_3 > CO_2 > CH_4 > H_2$   
c.  $CO_2 > NH_3 > H_2 > CH_4$   
d.  $CH_4 > CO_2 > NH_3 > H_2$

103. The coagulation of 200 ml of a positive colloid took place when 0.73 g HCl was added to it without changing the volume much. The flocculation value of HCl for the colloid is

- a. 150                    b. 100  
c. 36.5                  d. 10.0

104. Given below, catalyst and corresponding process/reaction are matched. The mismatch is

- a.  $[RhCl(PPh_3)_2]$  : hydrogenation  
b.  $TiCl_4 + Al(C_2H_5)_3$  : polymerization  
c.  $V_2O_5$  : Haber-Bosch process  
d. Nickel : hydrogenation

105. The capacity of an ion to coagulate a colloidal solution depends upon

- a. nature of charge  
b. amount of charge  
c. its shape  
d. both (a) & (b)

106. A graph of adsorption isobar of chemisorption shows that adsorption

- a. first decreases with temperature and then increases  
b. first increases with temperature and then decreases  
c. increases with temperature  
d. decreases with temperature

107. The gold numbers of some colloids are given below:

Colloid	Gold number
A	0.01
B	2.5
C	20

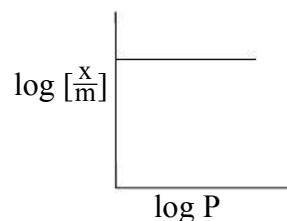
The protective nature of these colloids follows the order:

- a.  $A = B = C$               b.  $C > B > A$   
c.  $A > B > C$               d.  $B > A > C$

108. Which of the following is true in respect of adsorption?

- a.  $\Delta G < 0; \Delta S > 0; \Delta H < 0$   
b.  $\Delta G < 0; \Delta S < 0; \Delta H < 0$   
c.  $\Delta G > 0; \Delta S > 0; \Delta H < 0$   
d.  $\Delta G < 0; \Delta S < 0; \Delta H > 0$

109. Adsorption isotherm of  $\log \frac{x}{m}$  and  $\log P$  was found of the type:



This is true when :

- a.**  $P = 1$       **b.**  $\frac{1}{n} = \infty$   
**c.**  $\frac{1}{n} = 1$       **d.**  $P = 0$

- 110.** Langmuir's adsorption equation which describes the amount of gas adsorbed on a solid surface is written as

$$\frac{P}{x/m} = \frac{1}{ab} + \frac{p}{b}.$$

Here  $x/m$  is the extent of adsorption,  $a$  and  $b$  are constants, and  $p$  is the gas pressure.

On the basis of the above equation indicate which of the following statements is correct?

- (1) At low value of p  $x/m \propto p$

(2) At high value of p,  $x \rightarrow b$  (adsorption is independent of pressure).

(3) Between the low and high value of p, the above equation becomes  $x/m = kp^{1/n}$ , which is the Freundlich equation (here k and n are constants)

**a.** 1 and 2                    **b.** 2 and 3  
**c.** 1 and 3                    **d.** 1, 2 and 3

## **Multiple Correct Answer Type Questions**

- 111.** Which of the following factors are responsible for the increase in the rate of a surface catalysed reaction?

  - Adsorption increases the local concentration of reactant molecules on the surface of the catalyst
  - Heat of adsorption of reactants on a catalyst helps reactant molecules to overcome activation energy.
  - The catalyst increases the activation energy of the reaction.
  - A catalyst provides proper orientation for the reactant molecules to react.

**112.** Choose the incorrect statement for chemical adsorption

  - value of adsorption enthalpy is above  $-20.0 \text{ kJ mol}^{-1}$
  - Van der Waal's forces exist between adsorbent and adsorbate
  - usually monomolecular layer is formed on adsorbent
  - multimolecular layer may be formed on adsorbent

- 113.** Which colloid can not be coagulated by  $\text{Al}^{3+}$ ?

- a.** As<sub>2</sub>S<sub>3</sub>      **b.** CdS  
**c.** Haemoglobin      **d.** TiO<sub>2</sub>

- 114.** Although nitrogen does not adsorb on surface at room temperature, it adsorbs on the same surface at 83 K. Which one of the following statement is/are not correct?

- a. At 83 K, nitrogen molecules are held by chemical bonds.
  - b. At 83 K, nitrogen is adsorbed as atoms.
  - c. At 83 K, there is formation of monomolecular layer.
  - d. At 83 K, there is formation of multimolecular layer.

- 115.** Which of the following is/are correct about chemisorption?

- a. it is reversible in nature
  - b. it is specific in nature
  - c. it first increases with increase of temperature and then pressure
  - d. it involves the formation of a compound on the surface of the solid adsorbent.

- 116.** Which one of the following statements is /are correct?

- a. physical adsorption decreases with increase in the temperature
  - b. physical adsorption is multilayered
  - c. activation energy of physical adsorption is very high.
  - d. enthalpy change of physical adsorption is about  $20 \text{ kJ mol}^{-1}$ .

- 117.** Which is/are correctly matched?

- a. Faujasite (natural) –  
 $\text{Na}_{56}[(\text{Al}_2\text{O})_{56}(\text{SiO}_2)_{136}].250\text{H}_2\text{O}$
  - b. ZSM – 5 –  
 $\text{H}_x[(\text{AlO}_2)_x(\text{SiO}_2)_{96-x}].16\text{H}_2\text{O}$
  - c. Gemelinite –  $\text{Na}_2\text{Ca}(\text{AlO})_2(\text{SiO}_2)_4.6\text{H}_2\text{O}$
  - d. Anionic surfactant



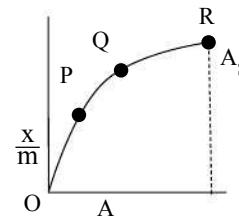
- 118.** Which is /are correct regarding the adsorption of a gas on surface of solid?

  - a. on increasing temperature adsorption increases continuously
  - b. enthalpy and entropy change is -ve

- c. adsorption is more for some specific substance  
d. It is reversible
- 119.** Which of the following is/are correct statement for physisorption?
- It is a reversible process
  - It requires less heat of adsorption
  - It is less specific.
  - It requires activation energy
- 120.** Which one of the following is/are true statement?
- Whipped cream is an example of foam.
  - Hair cream is an example of emulsion.
  - Cheese is an example of emulsion.
  - Cell fluid is an example of sol.
- 121.** Which among the following statements are correct with respect to adsorption of gases on a solid?
- The extent of adsorption is equal to  $kP^n$  according to Freundlich isotherm.
  - The extent of adsorption is equal to  $kP^{1/n}$  according to Freundlich isotherm.
  - The extent of adsorption is equal to  $(1 + bP)/aP$  according to Langmuir isotherm.
  - The extent of adsorption is equal to  $aP/(1 + bP)$  according to Langmuir isotherm.
- 122.** Which among the following statements is/are true?
- Increase of temperature may decrease the amount of adsorption
  - Increase of pressure increases the amount of adsorption
  - Particle size of the adsorbent will not affect the amount of adsorption
  - The adsorption may be monolayered or multilayered.
- 123.** Which of the following statements is/are correct?
- Ferric chloride solution is used to stop bleeding from fresh cut because it coagulates blood
  - The flocculation value of Arsenious sulphide sol is independent of the anion of the coagulating electrolyte
  - The smaller the gold number of a lyophobic colloid, the larger will be its protecting power
  - Lyophilic roots in contrast to lyophobic sols are easily coagulated on addition of small amount of electrolysis.
- 124.** The disperse phase in colloidal iron (III) hydroxide and colloidal gold is positively and negatively charged, respectively. Which of the following statements is/are correct?

- Magnesium chloride solution coagulates, the gold sol more readily than the iron (III) hydroxide sol
- Sodium sulphate solution causes coagulation in both sols
- Mixing of the sols has no effect
- Coagulation in both sols can be brought about by electrophoresis

**125.** In the given isotherm select the correct statements :



- nature of isotherm is different for two gases for same adsorbent
- $\frac{X}{m} \propto P^{1/n}$  along OP
- $\frac{X}{m} \propto P^0$  when point Q is reached
- $\frac{X}{m}$  does not increase as rapidly with pressure along QR due to less surface area available for adsorption

- 126.** Identify the incorrect statements regarding enzymes:
- enzymes are specific biological catalysts that cannot be poisoned
  - enzymes are specific biological catalysts that possess well defined active sites.
  - enzymes are specific biological catalysts that can normally function at very high temperatures ( $T - 1000\text{ K}$ ).
  - enzymes are normally heterogeneous
- 127.** Which of these statements regarding micelles is/are correct?
- The enthalpy of micelle formation in aqueous systems is slightly negative.
  - At critical micelle concentration, several properties of solution of surfactant such as molar conductivity, surface tension and osmotic pressure undergo a dramatic change.
  - Micelles from ionic surfactants can be formed only above a certain temperature called the Kraft temperature.
  - For soaps the cmc is  $10^{-4}$  to  $10^{-3}\text{ mol/l}$

## 10.26 ■ Surface Chemistry

128. Which of the following characteristics is/are correct for physical adsorption?
- Adsorption on solids is reversible
  - Adsorption is spontaneous
  - Both enthalpy and entropy of adsorption are negative
  - Adsorption increases with increase in temperature
129. Which of the following statements are correct here?
- Surface tension of lyophobic sols is similar to that of the dispersion medium
  - Electro-osmosis is the movement of the particles of dispersion medium under the influence of an electric field
  - On the application of an electric field, the particles of a lyophobic sol may move in either direction or not move at all.
  - Lyophilic colloid are easily precipitable
130. Which of the following properties are characteristic of lyophobic sols?
- Low viscosity
  - High viscosity
  - Reversibility
  - Coagulation by electrolytes at low concentration.
131. Which of the following is/are correct?
- Ferric chloride solution is used to stop bleeding from fresh cut because it coagulates blood
  - Lyophilic roots in contrast to lyophobic sols are easily coagulated on addition of small amount of electrolysis.
  - The smaller the gold number of a lyophobic colloid, the larger will be its protecting power
  - The flocculation value of Arsenious sulphide sol is independent of the anion of the coagulating electrolyte

### Linked-Comprehension Type Questions

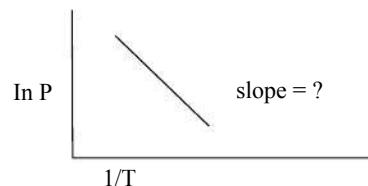
#### Comprehension 1

In physisorption the adsorbate is held to adsorbent by weak van der Waals forces, while in chemisorption, adsorbate is held to adsorbent by strong chemical bond. The extent of adsorption of a gas on a solid depends upon the nature of gas; nature of solid; specific area of the solid; pressure of gas; temperature of gas; and activation of adsorption. The relationship between the magnitude of adsorption ( $x/m$ ) and pressure of the gas at constant temperature is called

as adsorption isotherm. (Freundlich isotherm, and Langmuir isotherm)

132. Select the set of correct statements here?
- At 83 K  $N_2$  is physisorbed on the iron surface
  - At 773K and above  $N_2$  is chemisorbed on the iron surface
  - Potential energy is +ve in case of physisorption and zero in case for chemisorption
  - Potential energy is zero in case of physisorption and +ve in case for chemisorption
- (i), (ii), (iii)
  - (i), (ii), (iv)
  - (ii), (iii), (iv)
  - (i), (iv)
133. For the graph show below, which is the correct order of temperature?
- 
- a.  $T_1 > T_2 > T_3 > T_4$   
b.  $T_1 = T_2 = T_3 = T_4$   
c.  $T_1 < T_2 < T_3 < T_4$   
d.  $T_1 = T_2 > T_3 = T_4$

134. On plotting a graph between  $\ln P$  versus  $1/T$  as shown below, the slope is equal to



- $-\Delta H_{\text{Ads}}$
- $\Delta H_{\text{Ads.}}$
- $\frac{\Delta H_{\text{Ads.}}}{R}$
- R

#### Comprehension 2

The phenomenon of aggregation of colloid particles into an insoluble precipitate by the addition a suitable electro-

lyte (coagulating agent) is called coagulation. The minimum amount of an electrolyte (in millimoles) needed to cause it represents coagulation value. Coagulation power of an electrolyte depends upon the type and amount of charge present on ions of the electrolyte.

135. Which of the following will have the lowest coagulating value the colloid sol. formed by the peptization of  $\text{Sn}(\text{OH})_4$  by using little  $\text{NaOH}$  solution?
- $\text{SO}_4^{2-}$
  - $\text{PO}_4^{3-}$
  - $\text{Al}^{+3}$
  - $\text{Ca}^{2+}$
136. For the coagulation of  $\text{Fe}(\text{OH})_3$  sol the correct order of coagulation power can be given as
- $\text{Al}^{+3} > \text{Ba}^+ > \text{K}^+$
  - $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$
  - $\text{Cl}^- > \text{SO}_4^{2-} > \text{PO}_4^{3-}$
  - $\text{K}^+ > \text{Ba}^{+2} > \text{Al}^{+3}$
137. For the coagulation of a negatively charged colloid sol like  $\text{As}_2\text{S}_3$  two electrolytes  $\text{MgCl}_2$  and  $\text{AlCl}_3$  can be used. Whose coagulation values are 0.72 and 0.093 respectively. The coagulating power of  $\text{AlCl}_3$  is \_\_\_\_\_ times of that of  $\text{MgCl}_2$ .
- 0.129
  - 7.74
  - 3.37
  - 10.74

### Comprehension 3

Colloidal solution is heterogenous in nature having disperse phase and dispersion medium. There are 8 type of colloids. On the bases of interaction between disperse phase and dispersion medium colloids are classified as lyophilic and lyophobic. Lyophilic colloids act like protective colloids to protect the coagulation of lyophobic colloids and their protection power is measured in terms of Gold number (protection power  $\alpha 1/\text{Gold number}$ )

138. Which of the following is not correctly matched?

Dispersed phase	Dispersion medium	Example
a. Gas	Solid	dried sea foam
b. Solid	solid	Ruby glass
c. Liquid	gas	Mist
d. Liquid	solid	Cream

139. Which is not correctly matched here?

- Lyophilic sols -- more viscosity than the solvent
- Lyophobic sols -- surface tension is equal to that of medium

c. O/w type emulsion -- heavy metal salts of fatty acids

d. Micelle -- p - dodecyl benzene sulphonated

140. Which of the following represents the correct decreasing order of protecting power?
- Starch > potato starch > gelatin > gum arabic
  - Gelatin > gum arabic > potato starch > starch
  - Gelatin > gum arabic > starch > potato starch
  - Gum Arabic > gelatin > potato starch > starch

### Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given. Mark

- if A and R both are correct and R is the correct explanation of A.
- if A and R both are correct but R is not the correct explanation of A.
- A is true but R is false.
- A is false but R is true
- A and R both are false.

141. (A): Fluorescein is an adsorption indicator

(R): Fluorescein is a dye.

142. (A): A catalyst does not alter the equilibrium constant of a reaction.

(B): A catalyst forms a complex with the reactants and provides an alternate path with a lower energy of activation for the reaction. The forward and reverse reactions are affected to the same extent.

143. (A): For adsorption  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  all have –ve values.

(R): Adsorption is a spontaneous exothermic process in which randomness decreases due to force of attraction between adsorbent and adsorbate.

144. (A): When  $\text{AgNO}_3$  is treated with excess of potassium iodide, colloidal particles gets attracted towards anode.

(R): Colloidal particles adsorb common ions and thus become charged.

145. (A): When  $\text{SnO}_2$  is reacted with  $\text{NaOH}$ , then its sol. particles are attracted towards cathode.

(R): When  $\text{SnO}_2$  is reacted with  $\text{NaOH}$ , then it gives  $\text{SnO}_3^{2-}$  which is adsorbed by  $\text{SnO}_2$ , so it is negative charged sol.

## 10.28 ■ Surface Chemistry

146. (A): Isoelectric point is pH at which colloidal can move towards either of electrode.  
(R): At isoelectric point, colloidal solution become electrically neutral.
147. (A): AgI changes to positively charged colloidal sol in presence of KI.  
(R): It is due to adsorption of  $I^-$  on AgI.
148. (A): A catalyst can be poisoned by a small amounts of foreign substance  
(B): poison and reactants compete for the available catalyst surface.
149. (A): A colloid gets coagulated by addition of an electrolyte.  
(R): The rate of coagulation depends on the magnitude and sign of the charge of the coagulant ion.
150. (A): A gas with higher critical temperature gets adsorbed to more extent than a gas with lower critical temperature  
(R): The easily liquefiable gases get adsorbed to more extent which have higher critical temperature.
151. (A): In the presence of promoter, the activity of the catalyst is enhanced.  
(R): The promoter increases the surface area of the catalyst and thus, enhancing the number of active centers.
152. (A): The adsorption of a vapour on a clean surface is a spontaneous process.  
(R): Change in the entropy of the process is highly positive.
153. (A): In catalysis, the entire reaction occurs in a single phase.  
(B): Catalytic action of a surface depends on its absorption of the reactants.
154. (A): Proteins, starch and rubber are lyophilic colloids.  
(R): They have strong interaction with the dispersion medium.
155. (A): The rate of a reaction is accelerated by the presence of a catalyst.  
(B): The presence of a catalyst makes the value of  $\Delta G^\circ$  more negative
156. (A): Colloidal silver iodide is prepared by adding silver nitrate in slight excess to potassium iodide
- solution. When subjected to an electric field the colloidal particles migrate to the anode.  
(B): Colloidal particles absorb ions and thus become electrically charged.
157. (A): A catalyst enhances the rate of a reaction.  
(R): The energy of activation of the reaction is lowered in presence of a catalyst
158. (A): colloidal solution of cellulose nitrate cannot be prepared directly.  
(R): Lyophilic sols can be prepared directly by mixing the substance with the dispersion medium
- A colloidal solution of cellulose nitrate is obtained by obtained by dissolving.
159. (A): In the presence of promoter, the activity of the catalyst is enhanced.  
(R): The promoter increases the surface area of the catalyst and thus enhancing the number of active centers.
160. (A): Micelles are formed by surfactant molecules above the critical micellar concentration (CMC).  
(R): The conductivity of a solution having surfactant molecules decreases sharply at the CMC.

[IIT 2007]

### Matrix-Match Type Questions

161. Match the following:

**Column I**      **Column II**

- |           |                                    |
|-----------|------------------------------------|
| A. Milk   | (p) Dispersion phase is albumenoid |
| B. Cloud  | (q) Aquasol                        |
| C. Blood  | (r) Dispersed phase is water       |
| D. Starch | (s) Emulsion                       |

162. Match the following:

**Column I (Colloidal system)**      **Column II (example)**

- |                          |                        |
|--------------------------|------------------------|
| A. emulsifier            | (p) colloidal gel      |
| B. xerogel               | (q) dyes               |
| C. colloidal electrolyte | (r) foil of cellophane |
| D. purple cassius        | (s) dextrin            |

**163.** Match the following:

Column I	Column II
A. Physical adsorption	(p) $x/m = KP^{1/n}$
B. Chemisorption	(q) Bulk phenomenon
C. Fraundlich adsorption isotherm	(r) multilayered
D. Absorption	(s) unilayered
	(t) surface phenomenon

**164.** Match the following:

List I (Colloidal dispersion)	List II (Nature of dispersion)
A. Milk	(p). Solid in liquid
B. Clouds	(q). Liquid in gas
C. Paints	(r). Solids in solid
D. Jellies	(s). Liquids in liquid
	(t) Liquid in solid

**165.** Match the following:

Column I	Column II
A. Hydrophilic	(p) Water fearing
B. Hydrophobic	(q) Water loving
C. Suspension	(r) Liquid as suspension
D. Crystalloids	(s) True solutions

**166.** Match the following:

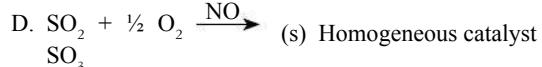
Column I	Column II
A. Geltatin	(p) - vely charged
B. $\text{Fe(OH)}_3$	(q) +vely charged
C. $\text{As}_2\text{S}_3$	(r) Lyophillic
D. Protien in acidic medium	(s) Lyophobic
	(t) Used in ice creams

**167.** Match the following:

Column I	Column II
A. Ammonia preparation	(p) biocatalysed

B. Hydrogenation (q) Fe

C. Fermentation (r) Ni



**168.** Match the following:

Column I	Column II
----------	-----------

A. Deacon's process for (p) finely divided iron with chlorine molybdenum as promoter

B. Hydrogenation of (q) copper (II) chloride vegetable oils

C. Ostwald's process (r) Finely divided nickel for nitric acid powder

D. Haber's process for (s) platinum gauze ammonia

**169.** Match the following:

Column I	Column II
----------	-----------

A. Coagulation (p) Scattering of light

B. Ultra filtration (q) washing of precipitates

C. Peptization (r) Purification of colloid

D. Tyndall effect (s) electrolyte

**170.** Match the following:

Column I	Column II
----------	-----------

A. Physisorption (p) Up take  $\text{rH}_2\text{O}$  by anhy.  $\text{CaCl}_2$

B. Chemisorption (q) Separation of inert gases on charcoal

C. Absorption (r)  $\text{H}_2$  on metal surface

D. Occlusion (s) Always endothermic

**171.** Match the following:

Column I	Column II
----------	-----------

A. Positive charge sol (p) Congo red

B. Langmuir adsorption (q) Charge on dispersion medium

C. Electro-osmosis (r) gelatin in acidic solution

D. Physiosorption (s) 200 – 400 kJ/mol

(t) reversible

**The IIT-JEE Corner**

172. Adsorption of gases on solid surface is generally exothermic because  
 a. enthalpy is positive  
 b. entropy decreases  
 c. entropy increases  
 d. free energy increases

[IIT 2004]

173. Rate of physisorption increases with  
 a. decrease in temperature  
 b. increase in temperature  
 c. decrease in pressure  
 d. decrease in surface area

[IIT 2004]

174. Which of the following is correct for lyophilic sol?  
 a. irreversible sol  
 b. formed from inorganic substances

- c. readily coagulated by addition of electrolyte  
 d. self stabilized

[IIT 2005]

175. Which of the following is correct for lyophilic sol?  
 a. irreversible sol  
 b. formed from inorganic substances  
 c. readily coagulated by addition of electrolyte  
 d. self stabilized

[IIT 2005]

176. Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient conditions is  
 a.  $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$   
 b.  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$   
 c.  $\text{CH}_3(\text{CH}_2)_6\text{COO}^-\text{Na}^+$   
 d.  $\text{CH}_3(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_3\text{Br}^-$

[IIT 2008]

**ANSWERS****Straight Objective Type Questions**

- |       |       |       |       |       |       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1. c  | 2. b  | 3. c  | 4. a  | 5. d  | 6. c  | 7. b  | 8. d  | 9. d  | 10. a | 11. a | 12. b |
| 13. a | 14. b | 15. c | 16. a | 17. b | 18. a | 19. b | 20. c | 21. b | 22. b | 23. b | 24. d |
| 25. a | 26. d | 27. a | 28. b | 29. b | 30. d | 31. d | 32. a | 33. c | 34. a | 35. b | 36. c |
| 37. c | 38. a | 39. d | 40. a | 41. d | 42. b | 43. c | 44. a | 45. d | 46. b | 47. b | 48. c |
| 49. d | 50. d | 51. c | 52. b | 53. b | 54. d | 55. c | 56. b | 57. a | 58. a | 59. c | 60. b |
| 61. b | 62. d | 63. b | 64. c | 65. b | 66. a | 67. d | 68. c | 69. c | 70. a | 71. a | 72. d |
| 73. b | 74. a | 75. a |       |       |       |       |       |       |       |       |       |

**Brainteasers Objective Type Questions**

- |        |        |        |        |        |        |        |        |        |        |        |       |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|
| 76. d  | 77. d  | 78. a  | 79. c  | 80. d  | 81. a  | 82. a  | 83. d  | 84. b  | 85. a  | 86. d  | 87. d |
| 88. a  | 89. b  | 90. d  | 91. a  | 92. a  | 93. a  | 94. d  | 95. c  | 96. c  | 97. c  | 98. b  | 99. a |
| 100. a | 101. a | 102. b | 103. b | 104. c | 105. d | 106. b | 107. c | 108. b | 109. c | 110. d |       |

**Multiple Correct Answer Type Questions**

- 111.** a, b, d    **112.** b, c, d    **113.** c, d    **114.** a, b, c    **115.** b, c, d    **116.** a, b, d    **117.** a, b, c  
**118.** b, c, d    **119.** a, b, c    **120.** a, b, d    **121.** b, d    **122.** a, b, d    **123.** a, b, c    **124.** a, b, d  
**125.** a, b, d    **126.** a, c, d    **127.** b, c, d    **128.** a, b, c    **129.** b, c    **130.** a, d    **131.** a, c, d

**Linked-Comprehension Type Questions****Comprehension 1**

- 132.** b    **133.** c    **134.** c

**Comprehension – 2**

- 135.** c    **136.** b    **137.** b

**Comprehension-3**

- 138.** d    **139.** c    **140.** b

**Assertion Reason Type Questions**

- |               |               |               |               |
|---------------|---------------|---------------|---------------|
| <b>141.</b> b | <b>142.</b> b | <b>143.</b> a | <b>144.</b> d |
| <b>145.</b> d | <b>146.</b> b | <b>147.</b> d | <b>148.</b> a |
| <b>149.</b> b | <b>150.</b> a | <b>151.</b> a | <b>152.</b> b |
| <b>153.</b> d | <b>154.</b> a | <b>155.</b> c | <b>156.</b> b |
| <b>157.</b> a | <b>158.</b> d | <b>159.</b> a | <b>160.</b> b |

**Matrix Match**

- 161.** A - (s), B - (q), C - (p), D - (q)  
**162.** A - (s), B - (r), C - (q), D - (p)  
**163.** A - (r, t), B - (s, t), C - (p), D - (q, t)  
**164.** A - (s), B - (q), C - (p), D - (t)  
**165.** A - (q), B - (p), C - (r), D - (s)  
**166.** A - (p, r, t), B - (q, s), C - (p, s), D - (q, r)  
**167.** A - (q), B - (r), C - (p), D - (s)  
**168.** A - (q), B - (r), C - (s), D - (p)  
**169.** A - (s), B - (r), C - (q), D - (p)  
**170.** A - (q, r), B - (r), C - (p, t), D - (s, r)  
**171.** A - (r, p), B - (s), C - (q), D - (t)

**The IIT-JEE Corner**

- 172.** b    **173.** a    **174.** d    **175.** d    **176.** a

**Hints and Explanations**

2. The movement of colloidal particles is known as electrophoresis or cataphoresis.
6. Cod liver is an example of water in oil emulsion.
7. The ability of a catalyst to accelerate the chemical reaction is known as its activity.
8. As the rubber has large molecular mass, therefore the solution of rubber is an example of macromolecular colloid.
9. The reactions in zeolites catalyst depend upon pores, apertures and size of cavities present in the catalysts.
10. The amount of gas physically on charcoal increases with pressure and decreases with temperature.
11. In smoke, a solid (carbon) is distributed in a gas (air). Since in this dispersion, the dispersed phase is solid and dispersion medium is gas, so it is a colloidal dispersion of a solid in gas.
12. Negative ions cause precipitation of a positively charged solute and vice versa, therefore addition of electrolyte is used for the destruction of colloids.
13. The colloidal solution of silver is prepared by Bredig's arc method. This process involves dis-

## 10.32 ■ Surface Chemistry

- persion as well as condensation of silver. In this method, electric arc is struck between electrodes of the silver immersed in the dispersion medium.
14. Tyndall effect is not observed in sugar solution. As sugar solution is a true homogeneous solution and when a beam of light is passed through its homogeneous solution placed in dark room, then it appears clear and this light is not scattered through it.
15.  $[\text{Fe}(\text{CN})_6]^{4-}$  have higher magnitude of charge i.e., 4, so they have minimum flocculation value.
16. The colloidal sulphur is used as germ killer, especially in plants, as it is easily absorbed by the plants.
17.  $\text{C}_6\text{H}_{12}\text{O}_6 \xrightarrow{\text{zymase}} 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2$
18. In homogeneous catalyst reactions, rate of reaction depends upon the concentration of catalyst.
19. The process of breaking an emulsion to yield the constituent liquid is called demulsification.
20. In positive adsorption the concentration of solute on the surface of the adsorbent becomes more.
22. NaCl has lower magnitude of opposite charge ( $\text{Na}^+$ ), so it has maximum flocculation value.
23. Dialysis is the process of separating the particles such as protein particles of colloids from the particles of crystalloids by means of diffusion.
24. Bleeding is stopped by the application of ferric chloride, as the blood is coagulated and the blood vessels are sealed.
25. The colloidal solution of silver bromide in gelatin is applied on glass plates or celluloid films or paper to form sensitive plates in photography.
26. Adsorption theory explains the mechanism of a reaction between two gases catalysed by a solid. And in this reaction, solid catalyst is used and reactants are in gaseous state. It is due to the mechanism of heterogeneous catalysis.
28. Smoke is an aerosol i.e. solid carbon particles dispersed in air.
29. As surface tension of a lyophilic sol is lower than that of the dispersion medium.
31. Such products are called auto catalyst.
32. Emulsifier is the substance is added to stabilizes the emulsion.
33. The colloidal antimony is commonly used in the treatment of eye disease also known as Kajal.
34. A has the least gold number, so it has the greatest protective value.
35. Concentration of electrolyte required to coagulate a given amount of  $\text{As}_2\text{S}_3$  sol is minimum in the case of aluminium nitrate.
36. Dialysis process can separate colloids (proteins) from crystalloids (glucose).
37. Solid aerosol involves solid dispersed in gas. e.g., smoke, storm etc.
38. Freundlich proposed a mathematical equation  
 $w/m = k P^{1/n}$
39. Occlusion is a process of adsorption of a gas by a solid such that the atoms or molecules of the gas occupy the interstitial position in solid lattice. Since hydrogen gas absorbed by palladium is a solid, so it is called occlusion.
40. Silica gel adsorbs the water vapours, so it is a case of adsorption.
46. Eosin is an organic dye, which is used as an indicator to detect the end point precipitation titration. In this process, at the end point +ve ions get adsorbed on precipitated molecules to form +ve species which combine with anions of the indicator. It changes colour of precipitate. So it is called adsorption indicator
47. Colloidal solutions are not purified by electrophoresis. It is a process which shows the existence of electrical charge which involves the movement of colloidal particles towards one or the other electrode when placed under the influence of an electric field.
48. Medicines are more effective, if they are used in colloidal state.
49. The artificial rain is caused by spraying oppositely charged colloidal dust over a cloud
50. Digestion of fats in the intestines takes place by the process of emulsification.
51. In lead chamber process,
- $$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \xrightarrow{\text{NO(g)}}$$
- $$2\text{SO}_3(\text{g})$$
52. The catalytic reaction, in which the catalyst is in a different phase from the reactant, is called heterogeneous catalysis.
53.  $\text{Mg} + \text{CH}_3\text{I} \xrightarrow{\text{Dry ether}}$   

$$\text{CH}_3\text{MgI}$$
55. As electrical disintegration or Bredig's arc method is used for preparing colloidal solution of metals like gold silver, platinum etc.
56. The aggregates of soaps or detergent molecules are called micelles.

61. This isotherm is based on the fact that every adsorption site is equivalent and that the ability of a particle to bind there does not depend upon near by sites.
62. In lead chamber process, the reactants ( $\text{SO}_2$  and  $\text{O}_2$ ) as well as the catalyst (NO) are all gases.
63. Pesticide spray is a colloidal dispersion of liquid in gas (an aerosol).
66. In Cottrell smoke precipitator, the smoke is allowed to pass through a chamber having a series of plates charged to very high potential ( 20000 to 70000 V) . Charged particles of smoke get attracted and by charged plates and the gas coming out of chimney precipitated become free of charged particles.
67. No. of miligrams =  $0.025 \times 1000 = 25$  So gold No. is also 25
68. Lyophilic sols are more stable than lyophobic sols because the residue left on evaporation can be readily transformed back into colloidal state simply by adding solvent.
69. Because exothermic nature of adsorption in equilibrium.
70. It is the example of homogeneous catalyst.

### Brainteasers Objective Type Questions

76. For true solution the diameter range is 1 to  $10\text{\AA}$  and for colloidal solution diameter range is 10 to  $1000\text{\AA}$ .
- $$\frac{V_c}{Vs} = \frac{(4/3)\pi r_c^3}{(4/3)\pi r_s^3} = \frac{r_c^3}{r_s^3}$$
- Ratio of diameters =  $(10/1)^3 = 10^3$
- $V_c/Vs \approx 10^3$ .
78. In Ziegler process, ethylene is passed under a pressure of 6 atmospheres at a temperature of 60 – 70°C into a suspension of titanium tetrachloride ( $\text{TiCl}_4$ ) and aluminium triethyl [ $\text{Al}(\text{C}_2\text{H}_5)_3$ ] in an inert solvent like heptane
79.  $\text{As}_2\text{S}_3$  is a negatively charged sol. The coagulating power of  $\text{Al}^{3+}$  ions will be maximum i.e. minimum amount will have to be added.
80.  $\log X/M = \log K + 1/n \log P$

$$\text{As } \frac{1}{n} = \tan 45^\circ$$

$$\text{So } n = 1$$

$$\text{As } \log K = 0.3010$$

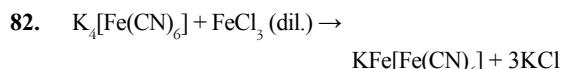
$$\text{So } K = 2$$

$$\text{Now } \frac{X}{M} = K \times p^n$$

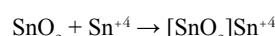
$$= 2 \times (0.4)^1$$

$$= 0.8$$

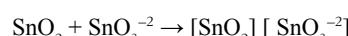
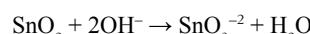
81. The diameter of colloidal particle ranges from  $10^{-9}$  to  $10^{-6}$  m.



85. As  $\text{Fe(OH)}_3$  sol is positively charged so anion with highest valency will be best coagulating agent i.e.  $[\text{Fe}(\text{CN})_6]^{3-}$ .



$\text{SnO}_2$  in alkaline medium forms negatively charged colloidal sol due to adsorption of  $\text{SnO}_3^{2-}$  ion



87. As  $0.25 \text{ g} = 250 \text{ mg}$  so according to definition gold number = 250.

88. Amount of colloid in mg = 2500 mg

2500 mg of protective colloid is required for 100 ml gold sol. For 10 ml of gold sol mass of protective colloid required is equal to 250 mg.

10 ml 10% NaCl coagulates 100 ml gold sol which is protected by 2500 mg of protective sol.

For gold number 1 ml 10 % NaCl is used for gold sol.

So gold number of protective colloid = 250

89. From the Freundlich isotherms that when pressure on a gas increases at constant temperature, then in the beginning, magnitude of its adsorption increases fast, then slowly and ultimately becomes independent of the pressure.

90. According to Freundlich equation,

$$\frac{X}{M} = KP^{1/n} \text{ or } \log \frac{X}{M} = \log K + \frac{1}{n} \log P$$

As Plot of  $\log x$  versus  $\log P$  is linear with slope  $= \frac{1}{n}$  and intercept  $= \log K$ .

$$\frac{1}{n} = \tan\theta = \tan 45^\circ = 1 \text{ or } n = 1$$

At  $P = 0.5 \text{ atm}$  and  $K = 10$

$$\frac{X}{M} = 10 \times (0.5)^1 = 5$$

$$\text{So, } x = 5 \text{ g}$$

## 10.34 ■ Surface Chemistry

92. As  $\log x/m = \log x + 1/n \log P$

$$\text{So } Y = C + mx$$

95. No. of molecules per gram of  $N_2$  in monolayer

$$= \frac{6 \times 10^{23}}{22,400} \times 1.33$$

$$= 3.582 \times 10^{19}$$

Cross-sectional area of a molecule

$$= 1.5 \times 10^{-19} \text{ m}^2$$

Area covered by molecules per gram

$$= 3.562 \times 10^{19} \times 1.5 \times 10^{-19}$$

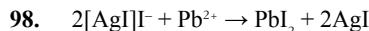
$$= 5.343 \text{ m}^2$$

So surface area =  $5.343 \text{ m}^2 \text{ g}^{-1}$

96. As  $Fe(OH)_3$  is positively charged so  $Cl^-$  ions with minimum opposite charge will have maximum flocculation value (minimum coagulating power).

97. As higher the gold number lesser will be the protective power of colloid.

$$\text{So } A < C < B < D$$



Thus 2 mol of  $[AgI]I^-$  has two mole-ve change it is equivalent to total charge on  $Pb^{2+}$  of one mole of  $Pb(NO_3)_2$ .

99.

101. 5 ml of 1M NaCl for coagulation = 5 millimoles

So 1000 ml (1L) of  $As_2S_3$  sol require NaCl for coagulation

$$= \frac{5}{100} \times 1000$$

$$= 50 \text{ millimoles}$$

Hence coagulation or flocculation value = 50.

102. Greater the critical temperature greater the adsorption.  $NH_3 > CO_2 > CH_4 > H_2$

103. As 200 mL of the sol require

$$= 0.73 \text{ g HCl}$$

$$= \frac{0.73}{36.5} \text{ mol} = 0.02 \text{ mol} = 20 \text{ m mol}$$

So 1000 mL (1L) of the sol will require

$$= \frac{20}{200} \times 1000 = 100 \text{ m mol.}$$

104. Haber-Bosch process is used for the synthesis of ammonia.



The best catalyst for this reaction is highly porous finely divided iron containing small amounts of promoters usually molybdenum or oxides of potassium and aluminium.

105. Coagulating value of an electrolyte is directly proportional to the valency of the active ions i.e., amount of charge, so capacity of an ion to coagulate a colloidal solution depends upon the nature and amount of its charge.

106. A graph of adsorption isobar of chemisorption shows that the adsorption first increases with temperature and then decreases. The initial increase is due to heat supplied, which acts as activation energy required in chemisorption, and the decrease afterwards is due to the exothermic nature of adsorption in equilibrium.

### Multiple Correct Answer Type Questions

114. At 83 K, there is physisorption and hence multilayered.

115. Chemisorption first increases with an increase of temperature and then decreases. But this process is irreversible in nature.

117. As



is a cationic surfactant

119. Physisorption does not require activation energy.

120. Cheese is a gel and not an emulsion.

122. As particle size of the adsorbent affects the amount of adsorption.

124. As Opposite charges attract each other So on mixing coagulation of two sols may be take place.

126. Normal optimum temperature of enzymes is between 25°C to 40°C. Enzymes have well defined active sites and their actions are specific in nature

127. The formation of micelles in aqueous solution is an endothermic process with very small but positive value of enthalpy of formation.

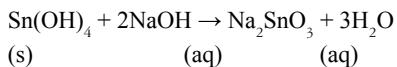
128. The temperature increases, the kinetic energy of adsorbate molecules. So physical adsorption takes place at low temperature

- 130.** Characteristic of lyophobic sols:

  - (i) Viscosity is same as of solvent
  - (ii) It is an irreversible solvent
  - (iii) Easily coagulated by addition of electrolytes.

## **Linked-Comprehension Type Questions**

135. Here  $\text{Sn}(\text{OH})_4$  adsorbs  $\text{SnO}_3^{2-}$  ions and becomes -vely charged so it can be coagulated by cation of the electrolyte. Here  $\text{Al}^{3+}$  has maximum +ve charged so it has maximum coagulation power.



$$\begin{aligned}
 137. \quad & \frac{\text{Coagulating power of AlCl}_3}{\text{Coagulating power MgCl}_2} \\
 & = \frac{\text{Coagulation value of MgCl}_2}{\text{Coagulation value of AlCl}_3} \\
 & = \frac{0.72}{0.093} \\
 & = 7.74
 \end{aligned}$$

138. As in cream both dispersed phase and dispersion medium are of liquids.

139. As heavy metal, salts of fatty acids are w/O type of emulsion.

160. The formation of micelles takes places only above a particular temperature called Kraft temperature ( $T_K$ ) and above a particular concentration called critical micelle concentration (CMC). Each micelle contains at least 100 molecules. Thus conductivity of the solution decreases sharply at the CMC.

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172. Adsorption of gas on solid is generally exothermic because on adsorption entropy decreases i.e., this factor opposes the process. For this process to be spontaneous, the energy factor must favour.

173. The physical adsorption i.e., physisorption is exothermic process, so on the basis of Le-Chatelier principle increasing of temperature is favourable towards a direction in which heat is absorbed, so the rate of physisorption increases with decrease of temperature.

176. Sodium Hexadecyl trimethylammonium Dodecylsulphate Bromide (CTAB)  
(SDS) CMC (mm)> – 10 1

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# CHAPTER 11

# Nuclear Chemistry

## Chapter Contents

Radioactivity: isotopes and isobars; properties of alpha, beta and gamma rays; Kinetics of radioactive decay (decay series excluded), carbon dating; stability of nuclei with respect to proton-neutron ratio; Brief discussion on fission and fusion reactions and Various level of multiple-choice questions.

## RADIOACTIVITY

Henry Becquerel observed that uranium minerals emit some peculiar rays which can effect a photographic plate even in dark. This property was called radioactivity and these rays were called radioactive rays (Becquerel rays). Radioactivity is defined as a nuclear property shown by atoms with unstable nucleus like U, Th, Ra etc., in which the nuclei of such elements undergo spontaneous disintegration without excitation by any external means. There are 33 element now which can show this property: Tc (transition metal), Pm (lanthanide) and all elements with atomic number more than 83, that is, Po, Ac, Rn, Fr, Ra etc.).

### REMEMBER

- Natural radioactivity and natural disintegration was given by Henry Becquerel.

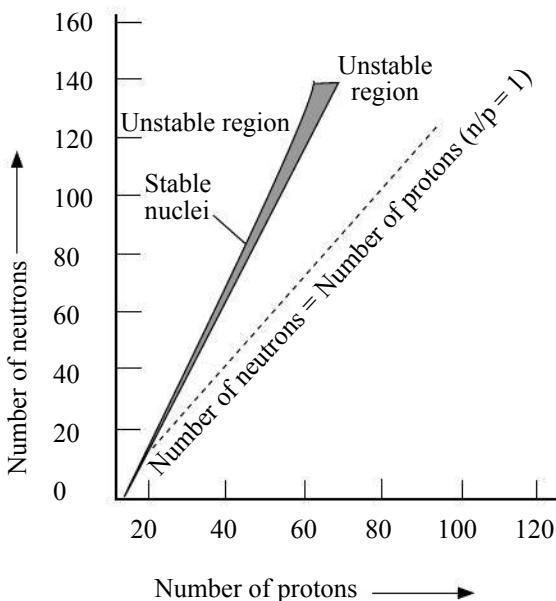
- Radioactivity was first observed in potassium uranyl sulphate  $K_2UO_2(SO_4)_2$ .
  - Artificial radioactivity was introduced by I.Curie and F.Jiolet.
- $$^{13}Al^{27} + {}_2He^4 \rightarrow {}_{15}P^{30} + {}_0n^1$$
- Marie Curie and Pierre Curie extracted Po, Ra from Pitch Blende [uranium ore ( $U_3O_8$ )] and introduced the word radioactive.
  - A radioactivity change is irreversible and liberates 1 million times more energy than a chemical change.
  - External factors (temperature, pressure etc.) do not affect radioactivity.
  - Radioactivity does not need activation energy.

## 11.2 ■ Nuclear Chemistry

### Units of Radioactivity

- 1 Curie =  $3.7 \times 10^{10}$  dis /sec
- 1 Rutherford =  $10^6$  dis /sec
- 1 Cr =  $3.7 \times 10^4$  Rutherford
- 1 Bq = 1 dis/sec
- 1 Gray (gy) = 1 kg tissue receiving one Joule of energy

### Reason for Unstable Nucleus or Radioactivity



#### Variation of number of neutrons with number of protons on stable non-radioactive nuclei.

1. n/p Ratio: The stable nuclei present within the zone of stability. All the nuclei falling outside this zone are invariably radioactive and unstable in nature. Nuclei that fall above the stability zone have an excess of neutrons while those present below have more protons. Both of these cause instability. These nuclei attain stability by making adjustment in the n/p ratio.
  - (a) n/p ratio  $> 1.5$  (Here  $\beta^-$ -emission occurs to decrease n/p ratio)
  - (b) n/p ratio  $< 1$  (Here  $\alpha$ -emission or positron emission or K-shell electron capture occurs to increase n/p ratio).
2. Low binding energy.
3. High value of packing fraction (Positive value of packing fraction means instability of the nucleus.).

### Mass Defect ( $\Delta m$ )

There is always a difference between the total mass of the protons and neutrons in a nucleus and the actual mass of the nucleus.

For example, for a stable  ${}^8\text{O}^{16}$  atom which contains eight protons, eight electrons and eight neutrons.

$$\begin{aligned}\text{Mass of } 8\text{p, } 8\text{n and } 8e \\= (8 \times 1.0073) + (8 \times 1.0087) + (8 \times 0.0005) \\= 16.132 \text{ amu}\end{aligned}$$

Actual mass of oxygen atom = 15.995 amu

So mass difference = 0.137 amu

The difference in mass is the net loss on forming a particular isotope from its constituent particles, is known as mass defect.

$$\Delta m = \text{Isotopic mass} - \text{Mass number}$$

### Binding Energy (B)

The stability of a nucleus is measured directly in terms of the binding energy per nucleon ( $\bar{B}$ ) which may be defined as the amount of energy released when the total number of nucleons (protons and neutrons) combine together to give the nucleus divided by the number of nucleons

According to Einstein's equation, the mass is converted into energy as follows:

$$E = mc^2$$

Here,

E = Energy produced

m = Loss of mass

c = Velocity of light

This energy is known as Binding Energy which is lost on forming the atom.

Binding energy is given as

$$B = \Delta m \times 931.5 \text{ MeV}$$

that is, binding energy is the energy equivalent of the mass defect

$$\bar{B} = \frac{B}{\text{Neutron or } (n + p)}.$$

Here  $\bar{B}$  is binding energy per nucleon.

### Packing Fraction

$$\text{Packing Fraction (f)} = \frac{\Delta m}{A} \times 10^4$$

Here A is mass number or atomic weight.

Stability  $\propto 1/f$  value

that is, positive value means instability.

## Illustrations

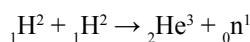
1. The mass defect for  $^{17}\text{Cl}^{35}$  is found to be 0.320 amu. Calculate the binding energy per nucleon.

**Solution** B.E. =  $\Delta m \times 931.48 \text{ MeV}$

$$= 0.320 \text{ amu} \times 931.48 \text{ MeV} = 298.07 \text{ MeV.}$$

$$\begin{aligned} \text{B.E./nucleons} &= \frac{\text{Total B.E.}}{\text{Number of nucleons}} \\ &= \frac{298.07}{35} = 8.516 \text{ MeV} \end{aligned}$$

2. Calculate the energy released in MeV and joules in the following nuclear reaction:



**Solution** Assume that the masses of  ${}_1\text{H}^2$ ,  ${}_2\text{He}^3$  and neutron are 2.0141, 3.0160 and 1.0087 a.m.u respectively.

$$\begin{aligned} \Delta_m &= 2 \times m_{{}_1\text{H}^2} - m_{{}_2\text{He}^3} + m_n \\ &= (2 \times 2.041) - (3.0160 + 1.0087) \\ &= 0.0035 \text{ a.m.u} \\ \Delta_E &= \Delta_m \times 931.48 \text{ MeV.} \\ &= 0.0035 \times 931.48 = 3260 \text{ MeV} \\ &= 5.223 \times 10^{-13} \text{ J} \\ (1 \text{ MeV}) &= 1.60 \times 10^{-13} \text{ J} \end{aligned}$$

3. In the fission of  ${}_{92}\text{U}^{235}$  with thermal neutron, the products are  $\text{Mo}^{95}$ ,  $\text{La}^{139}$  and two neutrons. If atomic masses (in amu) are: U = 235.118, Mo = 94.939, La = 138.950 and  ${}_0\text{n}^1$ , 1.009, calculate the energy released (MeV) in the fission of 1 g  $\text{U}^{235}$ .

**Solution**  ${}_{92}\text{U}^{235} + {}_0\text{n}^1 \rightarrow \text{Mo}^{95} + \text{La}^{139} + 2 {}_0\text{n}^1$



$$\text{Mass of Mo}^{95} + \text{La}^{139} + {}_0\text{n}^1$$

$$= 94.936 + 138.950 + 1.009$$

$$= 234.895 \text{ amu}$$

$$\text{Mass of } {}_{92}\text{U}^{235} = 235.118 \text{ amu}$$

$$\text{Mass defect} = 235.118 - 234.895 = 0.223 \text{ amu}$$

$$\Delta E = \Delta m \times 931.5$$

$$= 0.223 \times 931.5 = 207.7 \text{ MeV}$$

$$\text{Number of atoms in 1 g } {}_{92}\text{U}^{235}$$

$$= \frac{\text{Avogadro number}}{\text{Atomic mass}} \times \text{Mass}$$

$$= \frac{6.023 \times 10^{23}}{235} \times 1 = \frac{6.023 \times 10^{23}}{235 \text{ g}} \text{ atom}$$

$$\text{Energy released in the fission of } 1 {}_{92}\text{U}^{235} \text{ atom} = 207.7 \text{ MeV}$$

$$\text{Energy released in the fission of } \frac{6.023}{235} \times 10^{23} \text{ atoms}$$

$$= \frac{207.7 \times 6.023 \times 10^{23}}{235} \text{ MeV/}$$

$$= 5.32 \times 10^{23} \text{ MeV.}$$

4. Calculate the mass defect and binding energy per nucleon for an alpha particle whose mass is 4.0028 amu,  $m_p = 1.0073$  and  $m_n = 1.0087$  amu.

**Solution** Each  $\alpha$ -particle has 2p and 2n

$$\text{So mass of 2p + 2n in } \alpha\text{-particle}$$

$$= 2 \times (1.0073) + 2 \times (1.0087)$$

$$= 4.032 \text{ amu}$$

$$\text{As actual mass of } \alpha\text{-particle} = 4.0028 \text{ amu}$$

$$\text{Hence mass defect} = 4.032 - 4.0028 = 0.0292 \text{ amu}$$

$$\text{As B.E.} = \text{Mass defect} \times 931 \text{ MeV}$$

$$= 0.0292 \times 931 = 27.1852 \text{ MeV}$$

$$\text{Final B.E./nucleon} = \frac{27.1852}{4}$$

$$= 6.7963 \text{ MeV}$$

## Isotopes

Isotopes are the atoms of same element with same atomic number (Z) but different mass numbers (A). These were discovered by Soddy.

- Isotopes have same chemical properties.

- Isotopes have same number of proton.

- Rate of lighter isotopes > rate of heavy isotope (isotopic effect).

## 11.4 ■ Nuclear Chemistry

- Isotopes are separated by fractional distillation, thermal diffusion, and gaseous diffusion methods.
- Isotopes are detected by—Thomson parabola method, Asten's mass spectrograph method, Dempster method etc.

For example,

${}_1^1\text{H}$	${}_1^2\text{H}$	${}_1^3\text{H}$
$\text{C}_{12}$	$\text{C}_{14}$	
$\text{O}_{16}$	$\text{O}_{18}$	
$\text{Cl}_{35}$	$\text{Cl}_{37}$	

Heaviest isotope is radioactive in nature that is., C – 14, O – 18 etc.

### Isobars

Isobars are the atoms of different element with same mass number (A) but different atomic numbers (Z).

- They have different number of p, n but p + n is same.
- They have different chemical properties but physical properties related to mass are same.

Example –  ${}_{18}^{40}\text{Ar}$ ,  ${}_{19}^{40}\text{K}$ ,  ${}_{20}^{40}\text{Ca}$

### REMEMBER

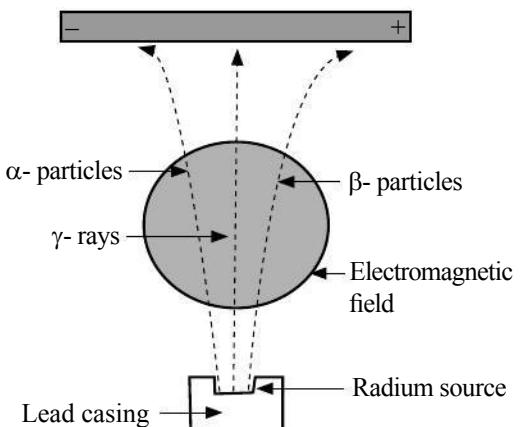
**Isotones** These have same number of neutrons.  
Example,

${}_6^{14}\text{C}$	${}_7^{15}\text{N}$	${}_8^{16}\text{O}$
n : 14-6	15-7	16-8
= 8	= 8	= 8

**Isodiapher** These are the atoms having same isotopic number or they have same (n – Z) or (A – 2Z) value.

Example,	${}_9^{19}\text{F}$	${}_{19}^{39}\text{K}$
	A : 19	A : 39
	Z : 9	Z : 19
	n : 10	n : 20
	n – Z = 1	n – Z = 1
	A – 2Z = 1	A – 2Z = 1

### Nature of Radiations



**Radiation from a radioactive element radium and the effect of a magnetic field on the same.**

Rutherford studied the properties of these radiations and these can be summarized as shown by the table.

### REMEMBER

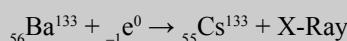
- α-particle emission occurs only when Z (atomic number) is greater than 82.
- β-particle emission occurs when neutron changes into proton  
$${}_0^1\text{n} \rightarrow {}_1^1\text{p} + {}_{-1}^0\beta$$
- When a proton changes into neutron position emission occurs.  
$${}_1^1\text{p} \rightarrow {}_0^1\text{n} + {}_{+1}^0\beta$$
- γ – rays has  $10^{10}$  more penetration power than α-rays.
- α, β, γ-Ray emission can be easily detected as they cause luminescence on the ZnS screen when placed on their way.

Properties	$\alpha$ -Particles or $\alpha$ -Rays	$\beta$ -Particles or $\beta$ -Rays	$\gamma$ -Rays
<b>Representation</b>	It is shown as helium nucleus or helium ions ${}_{2}^{4}\text{He}^+$ or $\text{He}^{++}$ .	It is shown as electron ${}_{-1}^{0}\text{e}^0$	It is shown as ${}_{0}^{0}\gamma^0$ .
<b>Charge and Mass</b>	It carries 2 units positive charge and 4 unit mass.	It carries 1 unit negative charge and no mass	These are electro magnetic rays with very short wavelength (app. 0.05 Å)
<b>Action of magnetic field</b>	These are deflected towards the cathode.	These are deflected anode.	These are not deflected.
<b>Velocity</b>	$2 \times 10^9 \text{ cm/s}$ or $2 \times 10^7 \text{ m/sec}$ (1/10 <sup>th</sup> to that of light)	2.36 to $2.83 \times 10^{10} \text{ cm/s}$ (2.36 to $2.83 \times 10^8 \text{ m/s}$ )	Same as that of light $3 \times 10^{10} \text{ cm/s}$ ( $3 \times 10^8 \text{ m/s}$ )
<b>Ionizing power</b>	Very high nearly 100 times to that of $\beta$ -rays.	Low nearly 100 times to that of $\gamma$ -rays.	Very low
<b>Penetrating power</b>	Low	100 times that of $\alpha$ -particles	10 times that of $\beta$ -particles
<b>Effect of ZnS plate</b>	They cause luminescence.	Very little effect	Very little effect
<b>Range</b>	Very small (8-12 cm)	More than of $\alpha$ -particles	More
<b>Nature of product</b>	Product obtained by the loss of one $\alpha$ -particle has atomic number less by 2 units and mass number less by 4 units	Product obtained by the loss of one $\beta$ -particle has atomic number more by one unit, without any change in mass number.	There is no change in the atomic number as well as in mass number.

**REMEMBER**

**K- Electron Capture** Here during a nuclear reaction to increase n/p ratio the nucleus of one of the atoms capture an electron from K-shell which converts proton to neutron. It is common in nuclei having  $Z > 70$ .

For example,

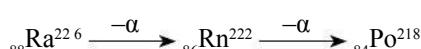


### Group Displacement Law

Group displacement law was introduced by Soddy, Fazan and Russel. According to this law:

- Only one type of particle is emitted at a time.
- When an  $\alpha$ -particle is emitted, the newly formed element will have atomic number less by two units and mass number less by four units while the group position is shifted two places towards the left.
- When a  $\beta$ -particle is emitted, the newly formed element will have the atomic number increased by one unit while mass number remains the same and the group position moves one place to the right.

For example,



Gp. No. IIA	Zero	VIA
-------------	------	-----

(2)	(0)	(16)
-----	-----	------



IVA	VA
(14)	(15)

No. of  $\alpha$ -particles

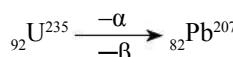
$$= \frac{\text{Loss in mass number}}{4}$$

No. of  $\beta$ -particles =  $2 \times \alpha \cdot [Z_1 - Z_2]$

Here  $Z_1$  = atomic number of parent element

$Z_2$  = atomic number of daughter element.

Example,

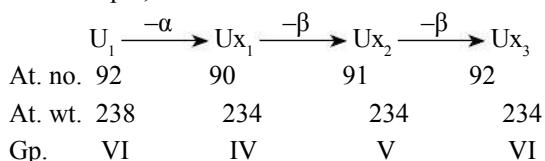


$$\text{Number of } \alpha\text{-particles} = \frac{235 - 207}{4} = 7$$

$$\begin{aligned} \text{Number of } \beta\text{-particles} &= 2 \times 7 - (92 - 82) \\ &= 4 \end{aligned}$$

- There is no effect of emission of  $\gamma$ -radiation on atomic number and mass number. It occurs when nucleus is excited for the purpose of minimizing energy that is, it is a secondary emission.
- After the successive emission of one  $\alpha$  and  $2\beta$  particles, an isotope is formed.

For example,



- In case of lanthanides and actinides, group position does not change after emission of  $\alpha$  or  $\beta$ -particles that is, it remains IIIB.

### Rate of Radioactive Disintegration and Disintegration Constant

The decay of a radioactive isotope takes place by the disintegration of the atomic nucleus. Rate of reaction does not depend upon external factors like temperature, pressure and amount or mass of substance.

$$\begin{aligned} \text{Rate of reaction} &= -\frac{dN}{dt} \\ &= -\frac{dN}{dt} \alpha N \end{aligned}$$

[ $N$  = Number of un-decayed atoms of the isotope present in the given amount of sample.]

$$-\frac{dN}{dt} = \lambda N$$

Here  $\lambda$  or  $K$  is decay constant.

$$\text{As } N = N_0 e^{-kt}$$

So

$$\lambda \text{ or } K = \frac{2.303}{t} \log_{10} \left( \frac{a}{a-x} \right) \text{ or } \frac{N_0}{N}$$

Here  $N_0$  or ' $a$ ' is initial amount or activity while  $a-x$  or  $N$  is activity or amount left after  $t$ -time.

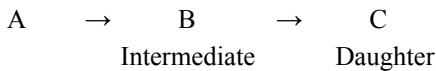
- $\lambda$  depends only upon half life period ( $t_{1/2}$ ). It does not depend upon the mass or amount of substance.

$$\lambda \propto \frac{1}{t_{1/2}}$$

$$\lambda \text{ or } K = \frac{0.693}{t_{1/2}}$$

### Radioactive Equilibrium or Steady State:

It is obtained when rate of formation of an element and its further disintegrations are the same.



$$\lambda_1 N_1 = \lambda_2 N_2$$

$$\frac{N_1}{N_2} = \frac{\lambda_2}{\lambda_1} = \frac{(t_{1/2})_1}{(t_{1/2})_2}$$

$$\frac{N_2}{N_1} = \frac{\lambda_1}{\lambda_2 - \lambda_1}.$$

It is a transient equation which is in fact a steady state.

### Half-life Period ( $t_{1/2}$ )

It is the duration in which a radioactive substance disintegrates half of its initial amount or left.

It can also be defined as the time required for the reactivity to drop to half its original value. Radioactive decay is a first order process.

The half-life is characteristic of a particular isotope and may vary from a fraction of a second to millions of years.

- It does not depend upon, mass, physical, chemical change and external factors.

$$t_{1/2} = \frac{0.693}{k \text{ or } \lambda}$$

$$T = n \times t_{1/2}$$

$$N = N_0 \times (\frac{1}{2})^n$$

Here  $n$  = Number of disintegrations.

### Average Life

It is the reciprocal of disintegration constant  $\lambda$ .

$$\tau = \frac{1}{K}$$

$$\tau = 1.44 \times t_{1/2}$$

### REMEMBER

Rate of disintegration or activity is given as

$$\frac{-dN}{dt} = \frac{0.693}{T} \times \frac{w \text{ (gm)}}{\text{mass no.}} \times 6.023 \times 10^{23}$$

$$\text{Amount decayed after } n = \frac{N_0 [2^n - 1]}{2^n}$$

### Illustrations

- Find the activity of 1.00 mg of radon, ( $Rn^{222}$ ) whose atomic mass is 222 u.

**Solution** The decay constant of  $Rn^{222}$  is given as

$$\lambda = \frac{0.693}{T_{1/2}}$$

$$= \frac{0.693}{(3.8 \text{ d}) \times (86400 \text{ s / d})} = 2.11 \times 10^{-6} \text{ s}^{-1}$$

The number  $N$  of atoms in 1.00 mg of  $Rn^{222}$  is given as

$$N = \frac{1.00 \times 10^{-6} \text{ Kg}}{(222 \text{ u}) \times (1.66 \times 10^{-27} \text{ Kg / u})}.$$

$$= 2.71 \times 10^{18} \text{ atoms}$$

So

$$R = \lambda \times N$$

$$= 2.11 \times 10^{-6} \times 2.71 \times 10^{18}$$

$$= 5.72 \times 10^{12} \text{ decays / s}$$

$$= 5.72 \text{ TBq}$$

$$= 155 \text{ Ci}$$

- What is the rate of disintegration (activity) of 0.001 g of a sample of  $Ra^{226}$  if,  $t_{1/2}$  is 1620 years?

**Solution** As  $t_{1/2} = \frac{0.693}{\lambda}$

$$\text{So } \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{1620 \times 365 \times 24 \times 60}.$$

As 226 g radius contains  $6.023 \times 10^{23}$  atoms.

So 0.001 g will contain

## 11.8 ■ Nuclear Chemistry

$$= \frac{6.023 \times 10^{23} \times 0.001}{226} \text{ atoms}$$

$$= 2.665 \times 10^{18} \text{ atoms}$$

$$\frac{-dN}{dt} = \lambda N$$

$$= 8.130 \times 10^{-10} \times 2.665 \times 10^{18} \text{ atoms min}^{-1}$$

$$= 2.167 \times 10^9 \text{ atoms min}^{-1}$$

7. Half-life period of iodine (atomic mass 125) is 60 days. Calculate the per cent of radioactivity remain after 120 days.

**Solution**  $t_{1/2} = 60 \text{ days}$  as  $t = 120 \text{ days}$

$$\text{As } n = \frac{T}{t_{1/2}} = \frac{120}{60} = 2$$

So per cent of radioactivity remain after 2 half lives

$$= \frac{N_0}{2^2}$$

$$= \frac{100}{4} = 25 \text{ per cent}$$

8. A sample of radioactive  $I^{133}$  gave with a GM counter 3150 counts per minute at a certain time and 3055 counts per minute exactly one hour later. What is the half life period of  $I^{133}$ ?

**Solution**  $N_0 = 3150$ ,  $N = 3055$ ,  $t = 1 \text{ hour}$

$$t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N}$$

$$= \frac{2.303}{1} \log_{10} \frac{3150}{3055} = 3.06 \times 10^{-2} \text{ year}^{-1}$$

$$t_{1/2} = \frac{0.693}{3.06 \times 10^{-2}} = 22.64 \text{ year}$$

9. At a certain instant, a piece of radioactive material contains  $10^{12}$  atoms. The half life of material is 30 days. Calculate the number of disintegrations in the first second.

**Solution**  $k = \frac{0.693}{t_{1/2}}$

$$t_{1/2} = 30 \text{ days}$$

$$k = \frac{0.693}{30 \times 24 \times 60 \times 60} \text{ sec}^{-1}$$

As  $N = 10^{12}$  atoms

$$-\frac{dN}{dt} = kN$$

$$-\frac{dN}{dt} = \frac{0.693 \times 10^{12}}{30 \times 24 \times 60 \times 60} \text{ sec}^{-1}$$

$$= 2.67 \times 10^5 \text{ sec}^{-1}$$

10. The activity of a radioactive isotope falls to 12.5 per cent in 90 days. Calculate the half life and decay constant of the radio isotope.

**Solution**  $k = \frac{2.303}{t} \log_{10} \frac{N_0}{N}$

$$k = \frac{2.303}{90} \log_{10} \frac{100}{25}$$

$$k = 23.03 \times 10^{-3} \text{ day}^{-1}$$

$$t_{1/2} = \frac{0.693}{23.03 \times 10^{-3}} = 30 \text{ days}$$

11.  $^{90}\text{Th}^{232}$  is an  $\alpha$ -particle emitter with a half life of  $1.4102 \times 10^{10}$  years. Given a 0.501 g sample of this thorium, how many  $\alpha$ -particles will it emit per second?

**Solution** As  $\lambda = \frac{0.693}{t_{1/2}}$

$$= \frac{0.693}{1.4102 \times 10^{10} \times 365 \times 24 \times 60 \times 60 \text{ sec}}$$

Number of Th-232 atoms in 0.5 g N

$$= N_0 \times \frac{w}{m}$$

$$= \frac{6.023 \times 10^{23} \times 0.5}{232}$$

As number of disintegration per second

$$= -\frac{dN}{dt} = k N$$

$$= \frac{0.693 \times 6.023 \times 10^{23} \times 0.501}{141.0 \times 10^{10} \times 365 \times 24 \times 60 \times 60 \times 232}$$

$$= 2023 \text{ disintegrations sec}^{-1}$$

As one Th-232 atom emits one alpha particle so number of  $\alpha$ -particles emitter per second = 2023.

12. A and B are in radioactive equilibrium and the ratio between the atoms of these elements is  $3.01 \times 10^8 : 1$  respectively. Half-life period of A is  $2.1 \times 10^{10}$  years, evaluate that of B.

**Solution** At radioactive equilibrium:

$$\frac{N_A}{N_B} = \frac{k_B}{k_A} = \frac{(t_{1/2})_A}{(t_{1/2})_B}$$

$$(t_{1/2})_B = (t_{1/2})_A \times \frac{N_B}{N_A}.$$

$$= 2.1 \times 10^{10} \times \frac{1}{3.01 \times 10^8} \\ = 69.76 \text{ years.}$$

13. What mass of  $C^{14}$  with  $t_{1/2} = 5730$  years has activity equal to one curie?

**Solution** 1 Curie =  $3.7 \times 10^{10}$  disintegration sec<sup>-1</sup>

$$\text{Rate} = 3.7 \times 10^{10} \text{ dps}$$

$$\text{Rate} = K \times \text{number of atoms}$$

$$3.7 \times 10^{10} = \frac{0.693}{5730 \times 365 \times 24 \times 60 \times 60}$$

$$\times \text{No. of atoms}$$

$$\text{No. of atoms}$$

$$= \frac{3.7 \times 10^{10} \times 5730 \times 365 \times 24 \times 60 \times 60}{0.693}$$

$$\text{No. of atoms} = 9.65 \times 10^{21}$$

$$\text{As } 6.023 \times 10^{23} \text{ atoms of } C^{14} \text{ weights} = 14 \text{ g}$$

$$\text{So } 9.65 \times 10^{21} \text{ atoms of } C^{14}$$

$$= \frac{14 \times 9.65 \times 10^{21}}{6.023 \times 10^{23}} = 0.2243 \text{ g}$$

14. It is known that 1 g of  $Ra^{226}$  emits  $11.6 \times 10^{17}$   $\alpha$ -particles per year. Given the half-life of  $Ra^{226}$  be 1600 years. Compute the value of Avogadro's number.

**Solution** As Rate =  $k \times N_0$

So 1 mole = 226 g Ra has Avogadro's No. atoms

$$\text{Hence 1 g Ra has} = \frac{\text{Avogadro no.}}{226}$$

$$\text{atoms} \times N_0$$

$$11.6 \times 10^{17} = \frac{0.693}{1600} \times \frac{\text{Av. No.}}{226}$$

$$\text{Avogadro's number} = 6.052 \times 10^{23}$$

15. Consider an  $\alpha$ -particle just in contact with a  $^{92}_{U^{238}}$  nucleus. Calculate the coulombic repulsion energy (i.e., the height of coulombic barrier between  $U^{238}$  and  $\alpha$ -particle) assuming that the distance between them is equal to the sum of their radii.

**Solution** As  $r(\text{nucleus}) = 1.3 \times 10^{-13} \times (A)^{1/3}$

$$\text{Here A is mass number or atomic weight}$$

$$\text{So } r(U^{238}) = 1.3 \times 10^{-13} \times (238)^{1/3}$$

$$= 8.06 \times 10^{-13} \text{ cm}$$

$$\text{Similarly } r(He^4) = 1.3 \times 10^{-13} \times (4)^{1/3}$$

$$= 2.06 \times 10^{-13} \text{ cm}$$

Hence total distance in between uranium and  $\alpha$ -nuclei

$$= 8.06 \times 10^{-13} + 2.06 \times 10^{-13} = 10.12 \times 10^{-13} \text{ cm}$$

$$\text{Repulsion energy} = \frac{Q_1 Q_2}{r}$$

$$= \frac{92 \times 4.8 \times 10^{-10} \times 2 \times 4.8 \times 10^{-10}}{10.12 \times 10^{-13}} \text{ erg}$$

$$= 418.9 \times 10^{-7} \text{ erg}$$

$$= 418.9 \times 10^{-7} \times 6.242 \times 10^{11} \text{ eV}$$

$$= \frac{418.9 \times 10^{-7} \times 6.242 \times 10^{11}}{10^6} \text{ MeV}$$

$$= 26.14 \text{ MeV}$$

16. A certain radioisotope  ${}_Z^A X^A$  (half-life = 10 days) decays to give  ${}_{Z-2}^{A-4} Y^{A-4}$ . If 1.00 g atom of  ${}_Z^A X^A$  is kept in a sealed vessel, how much helium will accumulate in 20 days? Express the result in  $\text{cm}^3$  at STP.

**Solution**  $\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{10 \text{ days}} = 0.0693 \text{ day}^{-1}$

$$A \log_{10} \frac{N_0}{N} = \frac{kt}{2.303}.$$

$$= \frac{0.0693 \times 20}{2.303} = 0.6018$$

$$\text{So } \frac{N_0}{N} = \text{Antilog } 0.6018 = 3.997$$

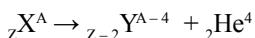
$$\text{Hence } N = \frac{N_0}{3.997} = \frac{1 \text{ g-atom}}{3.997}$$

## 11.10 ■ Nuclear Chemistry

So number of gram-atoms of X decomposed in 20 days

$$= 1 - \frac{1}{3.997} = \frac{2.997}{3.997} \text{ g-atom}$$

As the nuclear equation is



As the mass number decreases by 4 units and atomic number by 2 units,  $\alpha$ -particle is evolved during radioactivity.  $\alpha$ -particle then gets converted into helium atom. 1 g-atom of X emits 1 g-atom (1 mole) of  $\alpha$ -particles which get converted into 1 g-atom of helium gas. 1 g-atom (1 mole) of a gas occupies 22.4 litres at STP.

$$1 \text{ g-atom X} \equiv 1 \text{ g-atom He} \equiv 22.4 \text{ L} \equiv 22400 \text{ cm}^3$$

$$\text{So } \frac{2.997}{3.997} \text{ g-atom} \equiv \frac{22400 \text{ cm}^3}{1 \text{ g-atom}} \times \frac{2.997}{3.997}$$

g-atom

$$= 16796 \text{ cm}^3 \text{ at STP}$$

17. You have 0.1 gm atom of a radioactive isotope  ${}_zX^A$  (half-life = 5 days). How many number of atoms will decay during the eleventh day?

**Solution**  $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5 \text{ day}}$

$$\log_{10} \frac{N_0}{N} = \frac{kt}{2.3030} .$$

Here  $N_0$  = Initial number of radioactive atoms

$N$  = Number of radioactive atoms after time  $t$

$$N_0 = 0.1 \text{ gm atom} = 0.1 \text{ mol}$$

$$t = 10 \text{ days}$$

$$\log_{10} \frac{N_0}{N} = \frac{0.693 \times 10 \text{ days}}{5 \text{ days} \times 2.303} = 0.6018$$

$$\frac{N_0}{N} = \text{Antilog } 0.6018 = 3.997$$

$$N = \frac{N_0}{3.997} = \frac{0.1}{3.997} = 0.025 \text{ g-atom}$$

$$\text{At time } t = 11 \text{ days}$$

$$\log_{10} \frac{N_0}{N} = \frac{0.693 \times 11 \text{ days}}{5 \text{ days} \times 2.303} = 0.6620$$

$$\frac{N_0}{N} = \text{Antilog } 0.6620 = 4.592$$

$$N = \frac{N_0}{4.592} = \frac{0.1}{4.592} = 0.0218 \text{ g-atom}$$

Number of g-atom that disintegrates during the eleventh day

$$= 0.025 - 0.0218 = 0.0032 \text{ g-atom}$$

$$1 \text{ g-atom} = 6.023 \times 10^{23} \text{ atom/g-atom}$$

$$0.0032 \text{ g-atom} = 0.0032 \times 6.023 \times 10^{23} \text{ atoms}$$

$$= 1.927 \times 10^{21} \text{ atoms.}$$

18. Ten gram atoms of an  $\alpha$ -active radioisotope are disintegrating in a sealed container. In one hour the helium gas collected at STP is 11.2 cm<sup>3</sup>. Calculate the half-life of the radioisotope.

**Solution** As volume of helium gas collected at STP

$$= 11.2 \text{ cm}^3$$

So moles of helium gas

$$= \frac{11.2 / (1000 \text{ L})}{22.4 \text{ L}} \times 1 \text{ mol} = 0.0005 \text{ mol}$$

As initial amount of the radioisotope,

$$N_0 = 10 \text{ g-atom} = 10 \text{ mol}$$

Amount of radioisotope disintegrated  
= 0.0005 mol.

So amount of radioisotope that remains after 1 hour

$$= N = 10 - 0.0005 = 9.9995 \text{ mol}$$

$$\text{As } \log_{10} \frac{N_0}{N} = \frac{\lambda t}{2.303} .$$

$$\text{So } \lambda = \frac{2.303}{t} \log_{10} \frac{N_0}{N} = \frac{2.303}{1 \text{ hour}}$$

$$\log_{10} \frac{10}{9.9995} .$$

$$= 2.303 \times 0.0457 \text{ hour}^{-1}$$

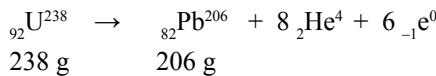
$$t_{1/2} = \frac{0.693}{\lambda} .$$

$$= \frac{0.693}{2.303 \times 0.0457 \text{ hour}^{-1}} = 6.584 \text{ hour.}$$

19.  ${}_{92}^{238}U$  by successive radioactive decay changes to  ${}_{82}^{206}Pb$ . A sample of uranium ore was analysed and found to contain 1.0 g of  ${}^{238}U$  and 0.1 g of  ${}^{206}Pb$ . Assuming that all the  ${}^{206}Pb$  had accumulated due to decay of  ${}^{238}U$ , find out the age of the ore. (Half life of  ${}^{238}U$  =  $4.5 \times 10^9$  years).

**Solution** As  $\lambda$  or  $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9 \text{ years}}$ .

The reaction is



As 206 g Pb obtained from 238 g U

So 0.1 g Pb is obtained from

$$= \frac{238}{206} \times 0.1 \text{ g} = 0.1155 \text{ gm of U-238}$$

So Initial mass of uranium ore =  $N_0$

$$= 1.0 + 0.1155 = 1.1155 \text{ g}$$

Mass of uranium ore, N, after t years = 1.0 g

Now apply

$$t = \frac{2.303}{k \text{ or } \lambda} \log_{10} \frac{N_0}{N_t \text{ or } N}$$

$$= \frac{2.303 \times 4.5 \times 10^9}{0.693} \log_{10} \frac{1.1155}{1.0}$$

$$= \frac{2.303 \times 4.5 \times 10^9}{0.693} \times 0.0476$$

$$= 7.1 \times 10^8 \text{ years}$$

20.  ${}_{84}^{210}\text{Po}$  decays with  $\alpha$ -particle to  ${}_{82}^{206}\text{Pb}$  with a half-life of 138.4 days. If 1.0 g of  ${}_{84}^{210}\text{Po}$  is placed in a sealed tube, how much helium will accumulate in 69.2 days? Express the answer in  $\text{cm}^3$  at STP.

**Solution**  $\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{138.4 \text{ days}} = 0.005 \text{ day}^{-1}$

$$\text{As } \log_{10} \frac{N_0}{N} = \frac{k t}{2.303} = \frac{0.005 \times 69.2}{2.303}$$

$$= 0.1502$$

$$\text{So } \frac{N_0}{N_t} = \text{Antilog } 0.1502 = 1.414$$

$$\text{Hence } N_t = \frac{N_0}{1.414} = \frac{1\text{g}}{1.414}$$

So amount of Po decomposed

$$= 1 - \frac{1}{1.414} = \frac{0.414}{1.414} \text{ g}$$

Moles of Po decomposed

$$= \frac{\text{Mass of Po decomposed}}{\text{Atomic mass of Po}}$$

$$= \frac{0.414 \text{ g}}{1.414 \times 210 \text{ g/mol}}$$

As 1 Po atom emits 1 alpha particle which gets converted into 1 helium atom

So 1 mol of Po emits 1 mole He gas

$$= \frac{0.414}{1.414 \times 210} \text{ mole emits}$$

$$= \frac{0.414}{1.414 \times 210} \text{ mol He gas}$$

As mole of He gas occupies  $22400 \text{ cm}^3$  at STP

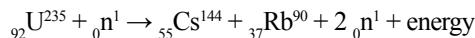
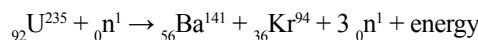
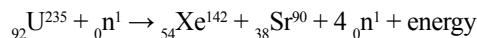
$$\text{So } \frac{0.414}{1.414 \times 210} \text{ mol He gas occupies}$$

$$= \frac{0.414 \times 22400 \text{ cm}^3}{1.414 \times 210} = 31.23 \text{ cm}^3 \text{ He at STP}$$

## Nuclear Fission

It was introduced by Otto Hahn and Strassman. It is the splitting of a heavy nuclei into two or more lighter nuclei with a evolution of huge amount of energy in the form of nuclear energy. This energy is due to mass defect.

Example,



- It occurs at low temperature than fusion
- Here less energy is released than fusion. It is noted by liquid drop method.
- It is a chain reaction which is of two types

## (A) Controlled Chain Reaction

Here chain reaction is controlled.

Example, nuclear reactor.

## Facts about Nuclear Reactor

- Fission material is U – 235, Pu – 239 and fertile material is U – 238.

## 11.12 ■ Nuclear Chemistry

- Here graphite, cadmium, beryllium, boron rods act as neutron absorber.
- Here heavy water works as moderator to slow down the speed of neutrons.
- Heavy water, polyphenyls, graphite act as coolant to remove excess of heat from the nuclear reactor.

### (B) Un-controlled Chain Reaction

Here, chain reaction can not be controlled.

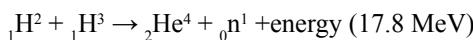
Example, atom bomb (U-235 or Pu -239)

### Nuclear Fusion

Here two or more lighter nuclei combine to form a heavy nuclei at a very high temperature ( $>10^6$  K) with evolution of a huge amount of energy in the form of nuclear energy. Here released energy is due to mass defect.

- Nuclear fusion is an exoergic reaction.

example.,



- It cannot be controlled and it is not a chain reaction.
- It occurs at high temperature, high pressure.

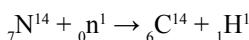
Example, H-bomb, Solar energy.

### Uses of Artificial Radioactive Isotopes

#### (1) Carbon Dating

It was introduced by W. S. Libby to find the age of fossils, old wood etc. with the help of C-14.

The principle reaction involved is



The ratio of C-14/C-12 in living things is  $1/10^{12}$ . There is one atom of C-14 for every  $7.49 \times 10^{11}$  carbon atom in  $\text{CO}_2$  of the atmosphere and in all living species.



$$t = \frac{2.303}{k \text{ or } \lambda} \log_{10} \frac{N_0}{N}$$

$$t = \frac{2.303 \times t_{1/2}}{0.693} \log_{10} \frac{N_0}{N}$$

Here  $t_{1/2}$  = Half life of C-14

$N_0$  = Original activity or amount or ratio of C-14/C-12 in fresh sample

$N$  = Final activity or amount or ratio of C-14 / C-12. in old or dead sample

### Illustrations

21. The  $_6\text{C}^{14}$  to  $_6\text{C}^{12}$  ratio in a piece of wood is 15 per cent that of the atmosphere. Calculate the age of the wood ( $t_{1/2}$  of  $_6\text{C}^{14}$  = 5580 years).

**Solution**  $t_{1/2} = \frac{0.693}{\lambda}$

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5580} = 1.242 \times 10^{-4} \text{ year}$$

$$\lambda = \frac{2.303}{t} \log_{10} \frac{C_0}{C_t}$$

Here  $t$  = age of the piece of the wood  $C_0$  or  $_6\text{C}^{14}$  to  $_6\text{C}^{12}$  ratio initially is 100 per cent

$$\lambda = \frac{2.303}{t} \log_{10} \frac{100}{15}$$

$$1.242 \times 10^{-4} = \frac{2.303}{t} \log_{10} \frac{100}{15}$$

$$t = \frac{2.303}{1.242 \times 10^{-4}} \log_{10} \frac{20}{3}$$

$$= \frac{2.303}{1.242 \times 10^{-4}} \times 0.8239$$

$$= 15280 \text{ years}$$

22. The bones of a prehistoric bison was found to have a C-14 activity of 2.80 dis/min.g carbon. Approximately how long ago did the animal live. Given  $A_0 = 15.3$  dis/min.g,  $t_{1/2} = 5730$  years?

**Solution**  $\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730} = 1.209 \times 10^{-4} \text{ year}^{-1}$

$$t = \frac{2.303 \log_{10} \frac{15.3}{2.80}}{1.209 \times 10^{-4}} = 14049 \text{ yrs}$$

23. A freshly cut piece of wood gives 16100 counts of  $\beta$ -ray emission per minute per kg and an old wooden bowl gives 13200 counts per minute per kg. Calculate the age of wooden bowl. The half life period of C-14 is 5568 years.

**Solution**  $\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5568} = 1.244 \times 10^{-4} \text{ year}^{-1}$

$$\begin{aligned} t &= \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N} \\ &= \frac{2.303}{1.244 \times 10^{-4}} \log_{10} \frac{16100}{13200} \\ &= 1596 \text{ years.} \end{aligned}$$

24. The half life period of  $C^{14}$  is 5760 year. A piece of wood when buried in the earth had 1 per cent  $C^{14}$ . Now as charcoal, has only 0.25 per cent  $C^{14}$ . How long has the piece of wood been buried?

**Solution**  $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5160} \text{ year}^{-1}$

$$k = \frac{2.303}{t} \log_{10} \frac{1}{0.25}.$$

$$\frac{0.693}{5760} = \frac{2.303}{t} \log_{10} 4$$

$$= \frac{2.303}{t} \times 2 \times 0.3010$$

$$t = \frac{2.303 \times 0.6020 \times 5760}{0.693}$$

$$= 11523.37 \text{ years}$$

25. An old wooden chair shows a  $_6C^{14}$  activity which is 80 per cent of the activity found today. Calculate the age of the sample. ( $t_{1/2}$  of  $_6C^{14}$  = 5770 years).

**Solution**  $t_{1/2}$  of  $_6C^{14}$  = 5770 years

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5770} \text{ year}^{-1}$$

$$k = \frac{2.303}{t} \log_{10} \frac{N_0}{N}$$

$$\frac{0.693}{5770} = \frac{2.303}{t} \log \frac{100}{80}$$

$$t = 1858.25 \text{ years.}$$

## (2) Rock Dating

It is based on the kinetics of radioactive decay. Here it is assumed that all the lead present in the sample

is due to decay of U-238. It is used to find the age of rocks, earth, minerals using U-238, Pb – 206

Here  $N_0$  = U-238 + Pb-206.

$N$  = U-238 i.e.,

$$t = \frac{2.303}{k \text{ or } \lambda} \log \frac{N_0}{N}$$

## Illustrations

26. Calculate the decay constant of uranium  $X_1$  from its half-life period. How long would it take for 30 per cent of an original sample to be decomposed?

**Solution** Half life for  $UX_1$  = 24.5 days

$$\lambda = \frac{0.693}{t_{1/2}}$$

For  $UX_1$

$$\lambda = \frac{0.693}{24.5} \text{ day}^{-1} = 2.829 \times 10^{-2} \text{ day}^{-1}$$

The decay constant is also given as

$$\ln \frac{N_t}{N_0} = -\lambda t$$

$$\ln \frac{N_0}{N_t} = \lambda t$$

$$t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N_t}$$

$$= \frac{2.303}{2.829 \times 10^{-2}} \log_{10} \frac{1.0}{0.7} = 12.61 \text{ days}$$

27. A sample of  $U^{238}$  (half life =  $4.5 \times 10^9$  year) ore is found to contain 23.8 g of  $U^{238}$  and 20.6 g of  $Pb^{206}$ . Calculate the age of the ore.

**Solution**  $N = U \text{ present} = \frac{23.8}{238} = 0.1 \text{ g atom}$

$$N_0 = U \text{ present} + U \text{ decayed}$$

$$= \frac{23.8}{238} + \frac{20.6}{238} = 0.1 + 0.1 = 0.2 \text{ g atoms}$$

$$\lambda = \frac{0.693}{4.5 \times 10^9} = 1.54 \times 10^{-10} \text{ year}^{-1}$$

$$t = \frac{2.303}{1.54 \times 10^{-10}} \log_{10} \frac{0.2}{0.1}$$

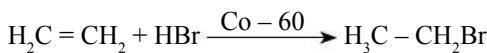
$$= 4.5 \times 10^9 \text{ year.}$$

### (3) In Medicines

- Na-24 ( $\gamma$ ) is used to detect tumor and blood clot.
- I – 131 ( $\beta$ ) is used in the treatment of thyroid gland.
- Co – 50 ( $\gamma$ ) is used to check cancer growth.
- Co – 60( $\gamma$ ) + Au – 198( $\gamma$ ) is used to check cancer, tumor treatment.
- P – 30 ( $\beta$ ) is used in the treatment of Skin diseases
- P – 32 is used in the treatment Leukemia

### (4) In Industry

Sb-124 is used to study the flow of petroleum through underground pipes.



### (5) In Agriculture

P-32 is used to trace the assimilation of phosphorous by plants.

### (6) Bio Processes (Tracer technique)

Photosynthesis is traced by O –18



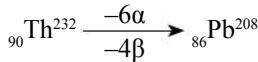
- C<sup>14</sup> is used to trace respiration by plants and to trace metabolism pathways in cells.

## Enhance Your Knowledge

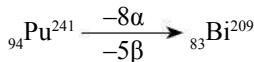
### Radio Active Disintegration Series

**4n (Thorium) Series:** Here mass number is divided completely by four.

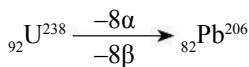
Example,



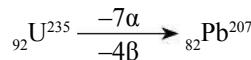
**4n+1 (Neptunium) Series:** Here remainder is one when mass number is divided by four. It is an artificial series and here end product is not lead.



**4n + 2 (Uranium) Series:** Here remainder is two when mass number is divided by four.

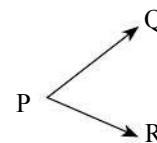


**4n + 3 (Actinium) Series:** Here remainder is three when mass number is divided by four.



### Parallel Path Decay

Suppose a radioactive element ‘P’ decays to ‘Q’ and ‘R’ in two parallel paths as follows:



Decay constant of ‘P’ = Decay constant of ‘Q’ + decay constant of ‘R’

$$\lambda_p = \lambda_q + \lambda_r$$

Here

$$\lambda_q = [\text{fractional yield of } Q] \times \lambda_p$$

$$\lambda_r = [\text{fractional yield of } R] \times \lambda_p$$

### Maximum Yield of Daughter Element

Let a radioactive element P decay to daughter element Q



$\lambda_p$  and  $\lambda_q$  are decay constants of P and Q. Maximum activity time of daughter element can be calculated as:

$$t_{\max} = \frac{2.303}{(\lambda_q - \lambda_p)} \log_{10} \frac{\lambda_q}{\lambda_p}$$

### Harkin’s Rule

According to Harkin’s Rule, elements of even atomic number (Z) are more stable and abundant than neighbouring element of odd ‘Z’.

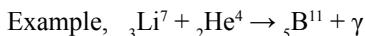
### Magic Number

Those elements which have 2, 8, 20, 28, 50, 82, 114 number of protons or 2, 8, 20, 28, 50, 82, 114, 126, 184 number of neutrons are quite stable and abundant in nature. These numbers are called magic numbers and the elements having these numbers do not show radioactivity

- Nuclear radius (r) of any atom is related to its mass number A as  $r = R_0 A^{1/3}$   
where  $R_0 = \text{constant} = 1.4 \times 10^{-15} \text{ m.}$

## Capture Reaction

If the particle used for bombardment is captured by the nucleus without release of any subsidiary particle, it is called capture reaction.

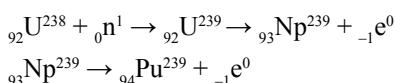


## Critical Mass

The minimum mass which the fissionable material must have for fission so that chain reaction continues at a constant rate is called critical mass. For U-235, it is 1-100 kg.

## Breeder Reactors

Breeder reactors are those reactors in which the neutrons produced from fission of U-235 are partly used to carry on the fission of U-235 and partly used to produce some other fissionable material E.g., Pu-235 from U-238.



## In Neutron Activation Analysis

It is used for finding the trace of one element present in another by activating the trace element by bombarding with neutrons. Example, traces of Ag present in a lead painting.

- Activity of a nucleus is inversely proportional to its half-life or average life. Thus shorter the half life of an element, greater is its radioactivity i.e., greater is the number of atoms disintegrating per second. It is called as Geiger–Nuttal rule.
- Every second, the sun loses  $4.3 \times 10^9$  kg of mass by fusion reactions i.e., a very huge amount of energy.

## Spallation

It was introduced by Seaborg. It is the splitting of a heavy nucleus into lighter nuclei by high energy particles. Here 10 to 20 neutrons are released.

Example,



## Solved Problems from the IITs

1. A small amount of solution containing  $\text{Na}^{24}$  radio nucleide with activity  $A = 2 \times 10^3$  dps was administered into blood of a patient in a hospital after 5 h, a sample of the blood drawn out from the patient showed an activity of 16 dpm per c.c.  $t^{1/2}$  for  $\text{Na}^{24} = 15$  hours.

Find (a) Volume of the blood in patient.

(b) Activity of blood sample drawn after a further time of 5 hour.

[IIT 1994]

## Solution

Suppose  $V$  ml blood is present in patient.

$$(A) r_0 \text{ of } \text{Na}^{24} = 2 \times 10^3 \text{ dps}$$

$$= 2 \times 10^3 \times 60 \text{ dpm}$$

$$= 120 \times 10^3 \text{ dpm for } V \text{ ml blood}$$

$$\text{Now } r \text{ of } \text{Na}^{24} = 16 \text{ dpm/ml (at } t = 5 \text{ hr })$$

$$= 16 \times V \text{ dpm/V ml}$$

$$\text{As } \frac{r_0}{r} = \frac{N_0}{N}$$

$$\text{So } \frac{N_0}{N} = \frac{120 \times 10^3}{16V}$$

$$\text{As } t = \frac{2.303}{K} \log_{10} \frac{N_0}{N}$$

$$\text{So } 5 = \frac{2.303}{0.693} \log_{10} \frac{120 \times 10^3}{16V}$$

On solving

$$V = 5.95 \times 10^3 \text{ ml.}$$

(B) Activity (X) of blood sample after 5 hours more

that is.,  $t = 10 \text{ hr}$

$$t = \frac{2.303}{K} \log_{10} \frac{N_0}{N}$$

$$10 = \frac{2.303}{0.693} \log_{10} \frac{120 \times 10^3}{X}$$

$$X = 75.6 \times 10^3 \text{ dpm per } 5.95 \times 10^3 \text{ ml}$$

## 11.16 ■ Nuclear Chemistry

$$= \frac{75.6 \times 10^3}{5.95 \times 10^3} \text{ dpm per ml}$$

$$= 12.71 \text{ dpm per ml}$$

$$= 0.2118 \text{ dps per ml}$$

2. One of the hazards of nuclear explosion is the generation of  $\text{Sr}^{90}$  and its subsequent incorporation in bones. This nucleide has a half life of 28.1 years. Suppose one microgram was absorbed by a new born child, how much  $\text{Sr}^{90}$  will remain in his bones after 20 years?

[IIT 1995]

**Solution**  $t_{1/2} = 28.1$  year

$$N_0 = 10^{-6} \text{ g}$$

$$t = 20 \text{ year}$$

$$N = ?$$

$$t = \frac{2.303}{k} \log_{10} \frac{N_0}{N}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1}$$

$$t = \frac{2.303 \times 28.1}{0.693} \times \log_{10} \frac{10^{-6}}{N}$$

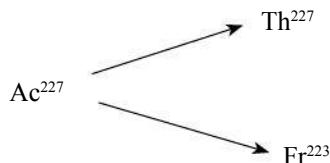
$$N = 6.1 \times 10^{-7} \text{ g}$$

3.  $\text{Ac}^{227}$  has a half life of 22 years with respect to radioactive decay. The decay follows two parallel paths, one leading the  $\text{Th}^{227}$  and the other leading to  $\text{Fr}^{223}$ . The percentage yields of these two daughter nuclides are 2 per cent and 98.0 per cent respectively. What is the rate constant in  $\text{year}^{-1}$ , for each of the separate paths?

[IIT 1996]

**Solution**  $K_{\text{Ac}} = \frac{0.693}{22} = 3.15 \times 10^{-2} \text{ year}^{-1}$

For the decay involving two parallel paths,



We have

$$K_{\text{Ac}} = K_{\text{Th Path}} + K_{\text{Fr Path}}$$

$$K_{\text{Ac}} \times \text{Fraction of Th} = K_{\text{Th Path}} \quad \dots \text{(i)}$$

$$K_{\text{Ac}} \times \text{Fraction of Fr} = K_{\text{Fr Path}} \quad \dots \text{(ii)}$$

$$\text{or } K_{\text{Ac}} \times (1 - \text{Fraction of Th}) = K_{\text{Fr Path}}$$

... (iii)

From equation (i) and (iii), we get

$$K_{\text{Ac}} = K_{\text{Th Path}} + K_{\text{Fr Path}}$$

$$\text{Thus, fractional yield of Th} = \frac{K_{\text{Th Path}}}{K_{\text{Ac Path}}}$$

$$K_{\text{Th Path}} = 3.15 \times 10^{-2} \times \frac{2}{100}.$$

$$= 6.30 \times 10^{-4} \text{ year}^{-1}$$

$$\text{Also fractional yield of Fr} = \frac{K_{\text{Fr Path}}}{K_{\text{Ac Path}}}$$

$$\text{So } K_{\text{Fr Path}} = 3.15 \times 10^{-2} \times \frac{98}{100}.$$

$$= 3.087 \times 10^{-2} \text{ year}^{-1}$$

4. With what velocity should an  $\alpha$ - particle travel towards the nucleus of a copper atom so as to arrive at a distance  $10^{-13}$  meter from the nucleus of the copper atom?

[IIT 1997]

**Solution** At closest distance kinetic energy should be equal should be equal to repulsion energy

$$\frac{1}{2} m u^2 = \frac{1}{4 \pi \epsilon_0} \times \frac{2 Z e^2}{r}$$

$$u^2 = \frac{Z e^2}{4 \pi \epsilon_0 m r}.$$

$$= \frac{29 \times (1.6 \times 10^{-19})^2}{3.14 \times 8.85 \times 10^{-12} \times (4 \times 1.672 \times 10^{-27}) \times 10^{-13}}$$

$$= 6.3 \times 10^6 \text{ m sec}^{-1}$$

5. (a) On analysis, a sample of uranium ore was found to contain 0.277 g of  ${}_{82}\text{Pb}^{206}$  and 1.667 g of  ${}_{92}\text{U}^{238}$ . The half life period of  $\text{U}^{238}$  is  $4.51 \times 10^9$  years, if all the lead were assumed to have come from decay of  ${}_{92}\text{U}^{238}$ , what is the age of earth?

- (b) An ore of  ${}_{92}\text{U}^{238}$  is found to contain  ${}_{92}\text{U}^{238}$  and  ${}_{82}\text{Pb}^{206}$  in the weight ratio of 1:0.1. The half life period of  ${}_{92}\text{U}^{238}$  is  $4.5 \times 10^9$  years. Calculate the age of ore.

[IIT 2000]

**Solution** Suppose Time = t year

$${}_{92}^{238}\text{U} = 1.667 \text{ g} = \frac{1.667}{238} \text{ mole}$$

$${}_{82}^{206}\text{Pb} = 0.277 \text{ g} = \frac{0.277}{206} \text{ mole}$$

As all the lead has come due to decay of  ${}^{238}\text{U}$  due to

$$\text{Mole of Pb formed} = \frac{0.277}{206}$$

$$\text{So mole of U decayed} = \frac{0.277}{206}$$

Hence total moles of uranium before decay

$$(N_0) = \frac{1.667}{238} + \frac{0.277}{206}$$

$$N \text{ for } {}^{238}\text{U} = \frac{1.667}{238}$$

$$\text{As } t = \frac{2.303}{K} \log_{10} \frac{N_0}{N}$$

$$= \frac{2.303 \times 4.51 \times 10^9}{0.693} \log_{10}$$

$$\frac{\frac{1.667}{238} + \frac{0.277}{206}}{\frac{1.667}{238}}$$

On solving

$$t = 1.143 \times 10^9 \text{ year}$$

$$(b) \text{ Here change in mass number } 238 - 206 = 32$$

As number of  $\alpha$ -particles emitted

$$= \frac{\text{Change in mass number}}{4}$$

$$= \frac{32}{4} = 8 \alpha$$

Number of  $\beta$ -particles = 2  $\alpha$  -  $[Z_1 - Z_2]$

$$= 2 \times 8 - [92 - 82] = 6$$

As 206 g of Pb is obtained from 238 g U.

So 0.1 g of Pb is obtained from

$$\frac{238}{206} \times 0.1 \text{ g} = 0.1155 \text{ g of U-235}$$

$$\text{Hence mass of uranium rock} = N_0 = 1 + 0.1155$$

$$= 1.1155 \text{ g.}$$

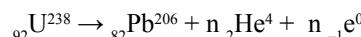
Now using

$$\begin{aligned} t &= \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N_t} \\ &= \frac{2.303}{0.693} \times 4.5 \times 10^9 \text{ years} \log_{10} \frac{1.1155}{1} \\ &= 7.0735 \times 10^8 \text{ years.} \end{aligned}$$

6. Calculate number of  $\alpha$ - and  $\beta$ -particles emitted when  ${}_{92}^{238}\text{U}$  changes into radioactive  ${}_{82}^{206}\text{Pb}$ .

[IIT 2000]

**Solution** Suppose  $n\alpha$  and  $n\beta$ -particles are given out during these change.



Equating mass number of both sides

$$238 = 206 + 4n + n \times 0$$

$$\text{So } n = 8$$

Equating atomic number on both sides

$$92 = 82 + 2n + n(-1)$$

$$= 82 + 2 \times 8 + 8 (-1)$$

$$\text{So } n = 6$$

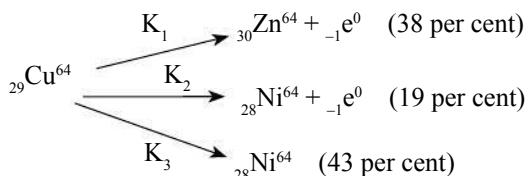
Number of  $\alpha$ -particles = 8

Number of  $\beta$ -particles = 6

7.  ${}^{64}\text{Cu}$  ( $t_{1/2} = 12.8$  hour) decays by  $\beta^-$ -emission (38 per cent)  $\beta^+$ -emission (19 per cent) and  $e^-$ -capture (43 per cent). Write decays product. Find  $t_{1/2}$  for each decays.

[IIT 2002]

**Solution** All this process can be shown as



$$\text{Here } K_{av} = \frac{0.693}{125.8} \text{ hr}^{-1}$$

$$\text{So } K_1 + K_2 + K_3 = K_{av}$$

$$= \frac{0.693}{12.8} = 5.41 \times 10^{-2} \text{ hr}^{-1} \quad \dots(i)$$

## 11.18 ■ Nuclear Chemistry

Also for parallel path decay  $K_1$ ,  $K_2$  and  $K_3$  are given as follows:

$$K_1 = \text{fractional yield of } {}_{30}\text{Zn}^{64} \times K_{\text{av}}$$

$$K_2 = \text{fractional yield of } {}_{28}\text{Ni}^{64} \times K_{\text{av}}$$

$$K_3 = \text{fractional yield of } {}_{28}\text{Ni}^{64} \times K_{\text{av}}$$

$$\text{So } \frac{K_1}{K_2} = \frac{38}{19} \quad \dots \text{(ii)}$$

$$\frac{K_1}{K_2} = \frac{38}{43} \quad \dots \text{(iii)}$$

From equation (i), (ii) and (iii) we get values of  $K_1$ ,  $K_2$  and  $K_3$

$$K_1 = 2.056 \times 10^{-2} \text{ hr}^{-1}$$

$$K_2 = 1.028 \times 10^{-2} \text{ hr}^{-1}$$

$$K_3 = 2.327 \times 10^{-2} \text{ hr}^{-1}$$

$$\text{Hence } t_{1/2} \text{ for } \beta^- \text{ emission} = \frac{0.693}{2.056 \times 10^{-2}}.$$

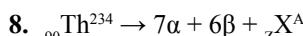
$$= 33.70 \text{ h}$$

$$t_{1/2} \text{ for } \beta^+ \text{ emission} = \frac{0.693}{1.028 \times 10^{-2}}.$$

$$= 67.41 \text{ h}$$

$$t_{1/2} \text{ for electron capture} = \frac{0.693}{2.327 \times 10^{-2}}.$$

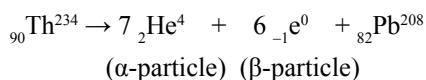
$$= 29.28 \text{ hr}$$



Identify the  ${}_z\text{X}^A$ .

[IIT 2004]

**Solution** On balancing the mass number and charge of the nuclear reaction, we obtain

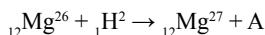


So  ${}_z\text{X}^A$  is  ${}_{82}\text{Pb}^{208}$ .

## MULTIPLE-CHOICE QUESTIONS

### Straight Objective Type Questions (Single Choice only)

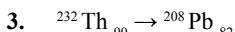
1. What is A in the following reaction?



- a.  ${}_{1}^{\text{H}}$
- b.  ${}_{0}^{\text{n}}$
- c.  ${}_{1}^{\text{D}}$
- d.  $\gamma$ -rays

2. Fission of nuclei is possible because the binding energy per nucleon in them

- a. Increases with mass number at high mass number.
- b. Decreases with mass number at high mass number
- c. increases with mass number of low mass.
- d. Decreases with mass number at low mass number



The number of  $\alpha$  and  $\beta$ -particle emitted during the above reaction is

- a.  $8\alpha$  and  $4\beta$
- b.  $8\alpha$  and  $16\beta$
- c.  $4\alpha$  and  $2\beta$
- d.  $6\alpha$  and  $4\beta$

4. Which of the following nuclides is especially stable?

- a.  ${}_{50}^{\text{Sn}}{}^{118}$
- b.  ${}_{82}^{\text{Pb}}{}^{208}$
- c.  ${}_{82}^{\text{Pb}}{}^{206}$
- d.  ${}_{81}^{\text{Tc}}{}^{209}$

5. Which of the following nuclides is most likely to decay by electron capture?

- a.  ${}_{80}^{\text{Hg}}{}^{195}$
- b.  ${}_{80}^{\text{Hg}}{}^{190}$
- c.  ${}_{80}^{\text{Hg}}{}^{205}$
- d.  ${}_{80}^{\text{Hg}}{}^{200}$

6. The atomic number A and mass number (M) of the nuclide formed when three  $\alpha$  and 2  $\beta$  particles are emitted from  ${}_{92}^{\text{U}}{}^{238}$ , is

- a. A = 88, M = 235
- b. A = 88, M = 226
- c. A = 87, M = 233
- d. A = 86, M = 226

7. The radioactive isotope  ${}^{60}_{27}\text{Co}$  which is used in the treatment of cancer can be made by (n, p) reaction. For this reaction the target nucleus is

- |                            |                            |
|----------------------------|----------------------------|
| a. ${}_{28}^{59}\text{Ni}$ | b. ${}_{27}^{59}\text{Co}$ |
| c. ${}_{28}^{60}\text{Ni}$ | d. ${}_{27}^{60}\text{Co}$ |

8. If the mass defect of a nuclide is  $3.32 \times 10^{-26}$  g, its binding energy is ..... MeV.

- a. 27.93
- b. 9.31
- c. 37.24
- d. 18.62

9. Which of the following notations shows the product incorrectly?

- a.  ${}_{5}^{\text{B}}{}^{10}(\alpha, n){}_{7}^{\text{N}}{}^{13}$
- b.  ${}_{96}^{\text{Cm}}{}^{242}(\alpha, 2n){}_{97}^{\text{Bk}}{}^{243}$
- c.  ${}_{7}^{\text{N}}{}^{14}(\text{n}, \text{p}){}_{6}^{\text{C}}{}^{14}$
- d. None of these

10. If the mass defect of  ${}_{4}^{\text{X}}{}^9$  is 0.090 amu, then binding energy per nucleon is (1 amu. = 921.5 MeV)

- a. 83.0 MeV
- b. 9.315 MeV
- c. 8.38 MeV
- d. 931.5 MeV

11. In which of the following decays, atomic number increases?

- a.  $\alpha$
- b.  $\lambda$
- c.  $\beta^-$
- d.  $\beta^+$

12. A radioisotope which is neutron poor and very heavy is most likely to decay by

- a. Electron capture
- b. Positron emission
- c. Alpha emission
- d. Beta emission

13. A heavy element has atomic number X and mass number Y. Correct relation between X and Y is

- a. X = Y
- b. X > Y
- c. X < Y
- d. X = Z(1 - Y)

14.  ${}^{222}_{86}\text{A} \rightarrow {}^{210}_{84}\text{B}$ . In this reaction, how many  $\alpha$  and  $\beta$  emissions have occurred?

- a. 3 $\alpha$ , 6 $\beta$
- b. 4 $\alpha$ , 3 $\beta$
- c. 3 $\alpha$ , 4 $\beta$
- d. 6 $\alpha$ , 3 $\beta$

## 11.20 ■ Nuclear Chemistry

15. The half lives of two radioactive nuclides A and B are 1 and 2 min. respectively. Equal weights of A and B are taken separately and allowed to disintegrate for 4 min. what will be the ratio of weights of A and B disintegrated?
- a. 1:2      b. 1 : 1  
c. 1:3      d. 5 : 4
16. Which type of radiation source would pose the greatest health risk when used internally for a medical procedure?
- a. A beta emitter,  $t_{1/2} = 6$  hours  
b. An alpha emitter,  $t_{1/2} = 6$  hours  
c. A beta emitter,  $t_{1/2} = 15$  days  
d. A gamma emitter,  $t_{1/2} = 6$  hours
17. In the nuclear fusion  ${}_1\text{H}^2 + {}_1\text{H}^2 \rightarrow {}_2\text{He}^4$ , the masses of  ${}_1\text{H}^2$  and  ${}_2\text{H}^4$  are 2.014 m<sub>u</sub> and 4.003 m<sub>u</sub> respectively. The energy released per atom of helium formed is ..... MeV.
- a. 4.31      b. 13.26  
c. 16.76      d. 23.275
18. As the mass number A varies which of the quantity related to nucleus does not change
- a. Density      b. Binding energy  
c. Volume      d. Mass.
19. In successive emission of  $\beta$  and  $\alpha$ -particles, how many  $\alpha$  and  $\beta$  particles should be emitted for the natural (4n + 1 series) conversion of  ${}_{94}\text{Pu}^{241}$  to  ${}_{92}\text{U}^{233}$ ?
- a. 2 $\alpha$ ,  $\beta$       b. 2 $\alpha$ , 2 $\beta$   
c. 2 $\alpha$ , 3 $\beta$       d.  $\alpha$ , 2 $\beta$
20. When  ${}_{66}\text{Dy}^{162}$  is formed by bombardment of  ${}_{64}\text{Gd}^{158}$ , what particle was used for the bombardment?
- a. two protons      b. four neutrons  
c. one  $\alpha$       d. two  $\beta^-$
21. What will be the binding energy of  $\text{O}^{16}$ , if the mass defect is 0.210 amu?
- a.  $1.89 \times 10^{10} \text{ J mol}^{-1}$   
b.  $1.89 \times 10^{12} \text{ J mol}^{-1}$   
c.  $1.89 \times 10^{13} \text{ J mol}^{-1}$   
d.  $1.89 \times 10^{14} \text{ J mol}^{-1}$
22. Consider two nuclei of same radioactive nuclide. One of the nuclei was created in a supernova explosion 5 billion years ago. The other was created in a nuclear reactor 5 minutes ago. The probability of decay during the next time is
- a. nuclei created in explosion decays first  
b. different of each nuclei  
c. independent of time of creation  
d. nuclei created in the reactor decays first
23. The compound used for the preparation of  $\text{UF}_6$  in the enrichment of  ${}_{92}\text{U}^{235}$  is
- a. HF      b.  $\text{CaF}_2$   
c.  $\text{ClF}_3$       d.  $\text{AlF}_3$
24. The half life of radioactive element is 160 days. The time for 15/16 disintegration is
- a. 280 days      b. 640 days  
c. 560 days      d. 2240 days
25. When  ${}_{13}\text{Al}^{27}$  is bombarded with  $\alpha$ -particle, a radioactive isotope of phosphorous  ${}_{15}\text{P}^{30}$  is formed. Which particle is emitted along with  ${}_{15}\text{P}^{30}$ ?
- a. deuteron      b. proton  
c. electron      d. neutron
26. Which of the following is not an advantage of fusion reactions over fission reactions for power generation?
- a. Ease of reaction initiation  
b. Fusion products are non polluting  
c. Cheap and plentiful fuel  
d. Fusion products are nonradioactive
27.  ${}_{1}\text{H}^1 + {}_{1}\text{H}^3 \rightarrow {}_{2}\text{He}^4$  this represent
- a.  $\beta$ -decay      b. fusion  
c. fission      d. none of these
28. For the nuclei with number > 100
- a. The nucleus essentially breaks up into two nuclides of equal mass releasing energy  
b. The two nuclei fuse to form a bigger nuclide releasing energy  
c. Binding energy of the nucleus increases on an average as A increases.  
d. Binding energy of the nucleus decreases on an average as A increases.
29. The projectile used to bombard  ${}_{7}\text{N}^{14}$  to get  ${}_{8}\text{O}^{17}$  and a proton is
- a.  ${}_{2}\text{He}^4$       b.  ${}_{0}\text{n}^1$   
c.  ${}_{1}\text{H}^1$       d.  ${}_{1}\text{H}^2$

- 30.** The phenomenon of radioactivity
- increases on applied pressure
  - is an exothermic change which increases or decreases with temperature
  - is a nuclear process does not depend upon external factors.
  - none of these
- 31.** The half life of a radioactive isotope is 1.5 hours. The mass of it that remains undecayed after 6 hours is (the initial mass of the isotope is 64 g.)
- 32 g.
  - 16 g.
  - 8 g.
  - 4 g.
- 32.** Which is more dangerous in terms of short-lived exposure to radiation? One mole of
- $^{94}\text{Sr}$ ,  $\beta^-$ ,  $t_{1/2} = 74$  seconds
  - $^{91}\text{Sr}$ ,  $\beta^-$ ,  $t_{1/2} = 9.8$  hours
  - $^{89}\text{Sr}$ ,  $\beta^-$ ,  $t_{1/2} = 50.4$  days
  - $^{90}\text{Sr}$ ,  $\beta^-$ ,  $t_{1/2} = 25$  years
- 33.** When a radioactive element emits successively one  $\alpha$ -particle and two  $\beta$ -particles, the mass number of the daughter element
- is reduced by 4 units
  - remains the same
  - is reduced by 2 units
  - is increased by 2 units
- 34.** The first trans-uranium element was synthesis by bombarding  $^{92}\text{U}^{238}$  with neutrons. After capturing one neutron, the resulting nuclide was unstable and decayed by beta emission. What was the product of these two nuclear reactions?
- $^{90}\text{Th}^{235}$
  - $^{92}\text{U}^{239}$
  - $^{93}\text{Np}^{239}$
  - $^{91}\text{Pa}^{239}$
- 35.** A nuclide of an alkaline earth metal undergoes radioactive decay by emission of the  $\alpha$ -particle in succession. The group of the periodic table to which the resulting daughter element would belong is,
- Gr 14
  - Gr 6
  - Gr 16
  - Gr 4
- 36.** Which of the following reaction represents  $^{22}\text{Ti}^{44}$  decay by electron capture?
- $^{22}\text{Ti}^{44} + {}_1\text{e}^0 \rightarrow {}_{21}\text{Sc}^{44}$
  - $^{22}\text{Ti}^{44} + {}_1\text{e}^0 \rightarrow {}_{23}\text{Ti}^{44}$
- 37.** The number of  $\alpha$  and  $\beta$ -particle emitted in the nuclear reaction  $^{228}_{90}\text{Th} \rightarrow {}^{212}_{83}\text{Bi}$  are
- $4\alpha$  and  $1\beta$
  - $3\alpha$  and  $7\beta$
  - $8\alpha$  and  $1\beta$
  - $4\alpha$  and  $7\beta$
- 38.** A shorthand way of writing transmutation equations is to show the bombarding particle and the subsequent emitted particle in parenthesis. Which particle is produced by  ${}^3\text{Li}^7(p, \alpha)$ ?
- ${}^4\text{Be}^{10}$
  - ${}^2\text{He}^4$
  - ${}^1\text{H}^4$
  - ${}^2\text{He}^3$
- 39.**  $^{92}\text{U}^{238}$  is radioactive and it emits  $\alpha$  and  $\beta$ -particles to form  $^{82}\text{Pb}^{206}$ . The number of  $\alpha$  and  $\beta$ -particles are respectively
- 8, 6
  - 6, 8
  - 4, 2
  - 8, 4
- 40.** When more than 3000 known nuclides are plotted on a neutron/proton grid they make up a group called
- The “sea of instability”
  - The “island of stability”
  - The “peninsula of nuclear stability”
  - None of these
- 41.** Mean life of radioactive sample is 100s and its half life in minutes is
- 1.155
  - $10^{-4}$
  - 1
  - 0.693
- 42.** If uranium (mass number 238 and atomic number 92) emits an  $\alpha$ -particle, the product has mass number and atomic number
- 234 and 90
  - 236 and 92
  - 238 and 90
  - 236 and 90
- 43.**  $^{57}_{27}\text{Co}$  will emit \_\_\_\_\_ radiation.
- electron capture
  - $\alpha$
  - $\beta^-$
  - $\beta^+$
- 44.** Which of the following is a fusion reaction?
- $^{98}_{98}\text{U} + {}_0^1\text{n} \rightarrow {}^{141}_{56}\text{Ba} + {}^{92}_{36}\text{Kr} + 3 {}_6^1\text{n}$
  - $^{92}_{92}\text{Fe} + {}_0^1\text{n} \rightarrow {}^{239}_{92}\text{U} + \text{Y}$
  - $^{26}_{26}\text{Fe} + {}_1^1\text{e}^0 \rightarrow {}^{55}_{25}\text{Mn}$
  - ${}^1_1\text{H} + {}^1_1\text{H} + 2 {}_0^1\text{n} \rightarrow {}^4_2\text{He} + \text{energy}$

## 11.22 ■ Nuclear Chemistry

45. The hyperfine lines in the spectrum is related to
- nuclear magnetic spin
  - Lande's splitting
  - Zeeman effect
  - Stark effect
46. Two radioactive elements A and B have decay constant  $\lambda$  and  $10\lambda$  respectively. If decay begins with the same number of atoms of the n, the ratio of atoms of A to those of B after time  $1/9\lambda$  will be
- $e^{-3}$
  - $e^2$
  - $e$
  - $e^{-1}$
47. Which of the following isotopes is the least stable?
- $^{240}\text{Pu}$ , 7.25 MeV/nucleon
  - $^{94}\text{Zr}$ , 8.64 MeV/nucleon
  - $^{7}\text{Be}$ , 5.37 MeV/nucleon
  - $^{23}\text{Na}$ , 8.11 MeV/nucleon
48.  $\alpha$ -particle emission is involved in
- $^{9}\text{F}^{17}$
  - $^{29}\text{Cu}^{67}$
  - $^{13}\text{Al}^{29}$
  - $^{84}\text{Po}^{214}$
49. How is the presence of radioactivity detected in a scintillation counter?
- By ionization of a gas
  - By interaction of the radiation with a photographic plate.
  - By fluorescence of ZnS upon interaction with radiation
  - By precipitate of a radioactive substance
50. The ionization power of  $\alpha$ ,  $\beta$  and  $\gamma$  radiations increases in the order
- $\beta < \alpha < \gamma$
  - $\alpha < \beta < \gamma$
  - $\gamma < \beta < \alpha$
  - $\alpha < \gamma < \beta$

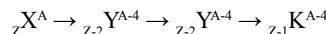
### Brainteasers Objective Type Questions (Single choice only)

51.  $^{92}\text{U}^{235}$ , nucleus absorbs a neutron and disintegrates into  $^{54}\text{Xe}^{139}$ ,  $^{38}\text{Sr}^{94}$  and x so. What will be the product x?
- 3-neutrons
  - 2-neutrons
  - $\alpha$ -particle
  - $\beta$ -particle
52. In the reaction  $^{2}_1\text{H} + ^{3}_1\text{H} \rightarrow ^{4}_2\text{He} + ^{1}_0\text{n}$ , if the binding energies of  $^{2}_1\text{H}$ ,  $^{3}_1\text{H}$  and  $^{4}_2\text{He}$  are respectively

a, b and c (in Me V) then the energy (in Me V) released is

- |                |                |
|----------------|----------------|
| a. $c + a - b$ | b. $c - a - b$ |
| c. $a + b - c$ | d. $a + b - c$ |

53. In the reaction represented by:



The decays in the sequence are

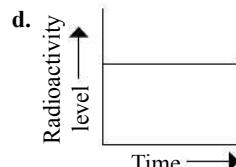
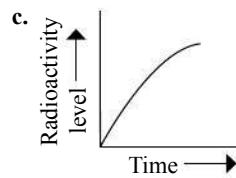
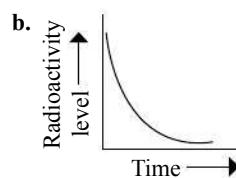
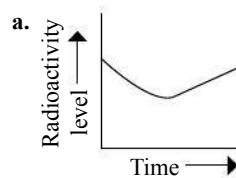
- |                            |                            |
|----------------------------|----------------------------|
| a. $\alpha, \beta, \gamma$ | b. $\beta, \gamma, \alpha$ |
| c. $\gamma, \alpha, \beta$ | d. $\alpha, \gamma, \beta$ |

54. For a radioactive element with  $\lambda = 2.2 \times 10^{-12} \text{ s}^{-1}$ , calculate the number of atoms that would show an activity of 10 mC.

[ $1\text{C} = 3.7 \times 10^{10}$  disintegrations per second]

- |                          |                          |
|--------------------------|--------------------------|
| a. $1.68 \times 10^{21}$ | b. $1.68 \times 10^{20}$ |
| c. $3.36 \times 10^{21}$ | d. $3.36 \times 10^{22}$ |

55. A radioactive form of phosphorous undergoes  $\nu$ -decay. What will the radioactivity level (R) versus time graph for the decay process appear?



- 56.** 1 g of radium is known to emit  $3.76 \times 10^{10}$  particle/sec. The half life period of radium is (atomic wt of Ra = 226)
- $3.7 \times 10^9$  s
  - $4.9 \times 10^{10}$  s
  - $1.41 \times 10^{10}$  s
  - $1.41 \times 10^{-11}$  s
- 57.** A piece of wood from an ancient artifact has a carbon-14 activity of 11.7 disintegrations per minute per gram of carbon. Current carbon-14 activity in fresh samples is 15.3 disintegrations per minute per gram of carbon. The half - life of carbon is 5715 years. Which of the statements is true?
- The rate constant for the decay is  $1.21 \times 10^4$  years.
  - The carbon -14 activity in the freshly cut sample is presumed to be different than in carbon dioxide in the air when doing calculations involving carbon -14 dating
  - The artifact could from the age of 2200 years nearly
  - The age of the sample is 1270 years.
- 58.** A binding energy curve is a plot of binding energy per nucleon versus atomic number. In what region of the binding energy curve are the most stable elements found?
- Binding energy is not dependent on atomic mass
  - In the lower right region (heavy atomic mass)
  - In the central top region (moderate atomic mass)
  - In the lower left region (low atomic mass)
- 59.** A radioactive substance having a half life of 3 days was received by 12 days. It was found that there were only 3g of the isotope in the container. The initial weight of the isotope when packed was
- 12 g
  - 24 g
  - 48 g
  - 96 g
- 60.** The mass of helium atom of mass number 4 is 4.0026 amu; while that of neutron and proton is 1.0087 and 1.0078 respectively in teh same scale. Hence, the nuclear binding per nucleon in the helium atom is
- 7.18 MeV
  - 6.18 MeV
  - 8.18 MeV
  - 9.18 MeV
- 61.** Consider  ${}_{13}^{25}\text{Al} \rightarrow {}_{12}^{25}\text{Mg} + {}_{+1}^0\text{e}^- + \nu$
- $$m_{\text{Al}} = 24.990423 \text{ u};$$
- $$m_{\text{Mg}} = 24.48539 \text{ u}.$$
- Find the Q value of reaction.
- a.** 5.3 MeV      **b.** 2.3 MeV  
**c.** 3.3 MeV      **d.** 1.3 MeV
- 62.** In natural radioactive disintegration, U-238 emits one  $\alpha$  and two  $\beta$  and then five  $\alpha$ - particle successively. The end product obtained is
- ${}_{82}^{82}\text{Pb}^{218}$
  - ${}_{82}^{82}\text{Pb}^{214}$
  - ${}_{84}^{84}\text{Pb}^{218}$
  - ${}_{82}^{82}\text{Pb}^{216}$
- 63.**  ${}_{11}^{22}\text{Na}^{22}$  has a half-life of 2.68 years. It decays both by positron emission and electron capture with a ratio of 86 % of the former to 11 % of the latter. What is the half-life for positron emission?
- 3.11 years
  - 6.22 ears
  - 3.44 years
  - 4.29 years
- 64.** The nucleus resulting from  ${}_{92}^{92}\text{U}^{238}$  after successive emission of two  $\alpha$ - and four  $\beta$ -particle is
- ${}_{90}^{90}\text{Th}^{230}$
  - ${}_{92}^{92}\text{U}^{230}$
  - ${}_{88}^{88}\text{Ra}^{230}$
  - ${}_{94}^{94}\text{Pu}^{230}$
- 65.**  ${}_{57}^{57}\text{Co}$  decays by electron capture. Its half life is 272 days. Find the activity left a year if present activity is  $2 \mu\text{ Ci}$ .
- 0.39  $\mu\text{ Ci}$ .
  - 0.431  $\mu\text{ Ci}$ .
  - 0.788  $\mu\text{ Ci}$ .
  - none of these
- 66.** Half-life of radioactive  ${}^{14}\text{C}$  is 5760 years. In how many years, 200 mg of  ${}^{14}\text{C}$  will be reduced to 25 mg?
- 5760 years
  - 11520 years
  - 17280 years
  - 23040 years
- 67.** A radioactivity sample decays in two modes. In one mode its half life is  $t_1$  and in the other mode its half life is  $t_2$ . Find the overall half life.
- $\frac{t_1 + t_2}{2}$
  - $\frac{t_1 t_2}{t_1 + t_2}$
  - $t_1 + t_2$
  - $\frac{t_1 t_2}{t_1 - t_2}$
- 68.** A nucleus with 70 neutrons has a neutron-to proton ration less than one. How can it gain stability?
- Alpha decay
  - Beta decay
  - Electron capture
  - Gamma emission
- 69.** A sample of radioactive substance gave 530 counts per minute and 510 counts per minute at times differing by 1 hour. The decay constant ( $\lambda$ ) in  $\text{min}^{-1}$  is given by

**11.24** ■ Nuclear Chemistry

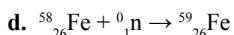
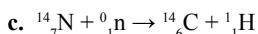
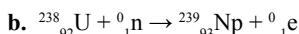
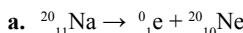
a.  $\lambda = \frac{530}{510} \times 60$

b.  $e^{60\lambda} = \frac{530}{510}$

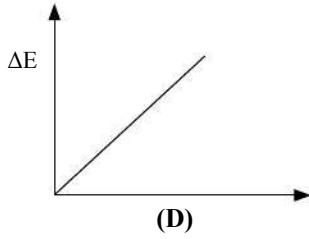
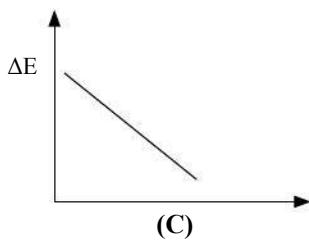
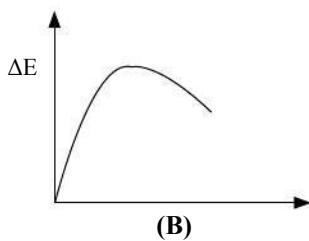
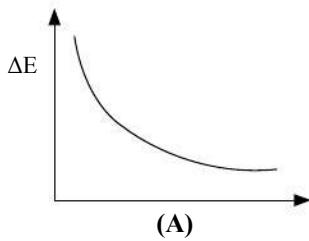
$$\text{c. } \lambda = \frac{2.303}{60} \log \frac{510}{530}$$

d.  $\lambda = \frac{2.303}{60} \times \frac{530}{510}$

- 70.** Which of the following represents the preparation of a transuranium element?



71. The curve between binding energy per nucleon ( $E$ ) and mass number  $A$  is



- 72.** The total binding energies for  ${}^3\text{He}$ ,  ${}^4\text{He}$  and  ${}^6\text{He}$  are 7.72, 28.29 and 29.26 MeV respectively. Arrange the 3 isotopes in increasing order of binding energy per nucleon.

  - ${}^4\text{He} < {}^3\text{He} < {}^6\text{He}$
  - ${}^3\text{He} < {}^6\text{He} < {}^4\text{He}$
  - ${}^3\text{He} < {}^4\text{He} < {}^6\text{He}$
  - ${}^6\text{He} < {}^4\text{He} < {}^3\text{He}$

**73.** The radioisotope, tritium ( ${}^1_3\text{H}$ ) has a half life of 12.3 years. If the initial amount of tritium is 32 mg, how many milligrams of it would remain after 49.2 years?

  - 4 mg
  - 8 mg
  - 1 mg
  - 2 mg

**74.** There are two radio nuclei P and Q. P is  $\alpha$ -emitter and Q is a  $\beta$ -emitter, their decay constant are in the ratio of 1 : 2. What should be the number of atoms two at time  $t = 0$ , so that probability of getting of  $\alpha$ - and  $\beta$ -particles are same at time  $t = 0$ ?

  - 1 : 2
  - 2 : 1
  - 1 : 4
  - 4 : 1

**75.** A radioactive isotope decays at such a rate that after 192 minutes only 1/16 of the origin amount remains. The half life of the radioactive isotope is

  - 12 min
  - 24 min
  - 32 min
  - 48 min

**76.** Consider fusion of He plasma. At what temperature fusion at a distance 2 fm is possible?

  - $2.23 \times 10^8\text{K}$
  - $2.23 \times 10^9\text{K}$
  - $2.23 \times 10^{10}\text{K}$
  - $2.23 \times 10^{11}\text{K}$

**77.** A radioactive isotope has half life of 8 days. If today 125 mg is left over, what was its original weight 32 days earlier?

  - 2 g
  - 4 g
  - 5 g
  - 6 g

**78.** The half life of a radio-isotope is three hours. If the mass of the undecayed isotope at the end of 18 hours is 3.125 gm, what was its mass initially?

  - 300 g
  - 200 g
  - 180 g
  - 400 g

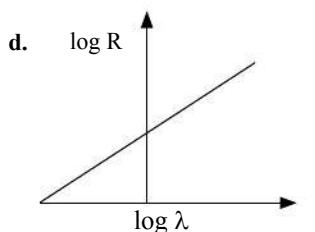
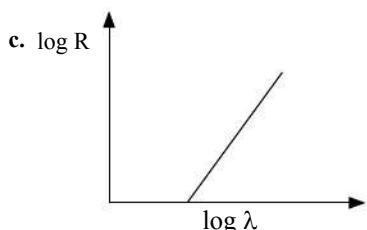
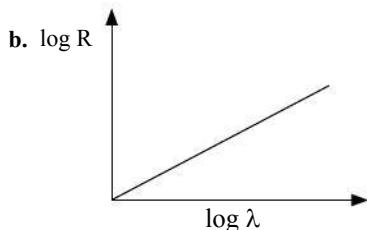
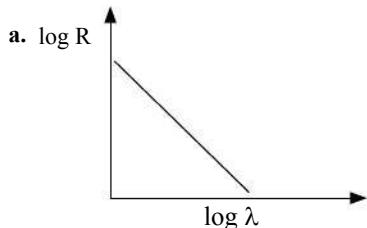
**79.** The number of  $\beta$ -particles emitted during the change  ${}_a\text{M}^c \rightarrow {}_d\text{N}^b$  is

  - $d + \frac{[(c - b)]}{2} - a$
  - $d + \frac{[(a - b)]}{2} - c$

c.  $d + \frac{[(a-b)]}{2} + c$

d.  $\frac{a-b}{4}$

80. According to Geiger - Nuttal law the curve between  $\log \lambda$  and  $\log R$  will be



81. A wooden box excavated from Indus valley had an activity of 9.3 disintegration per minute per gm of carbon. What is the approximate age of this civilization?

- a. 7800 years      b. 8100 years  
c. 9200 years      d. 8500 years

82. At radioactive equilibrium, the ratio between the atoms of two radioactive elements X and Y was found to be  $3.1 \times 10^9 : 1$  respectively. If  $T_{50}$  of the element X is  $2 \times 10^{10}$  years, then  $T_{50}$  of the element Y is

- a. 6.45 years  
b.  $3.1 \times 10^6$  years  
c.  $6.2 \times 10^7$  years  
d.  $21 \times 10^8$  years

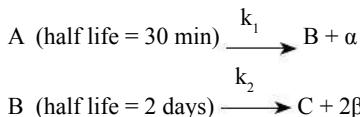
83. What weight of  $C^{14}$  will have radioactivity one curie if  $\lambda$  (disintegration constant) is  $4.4 \times 10^{-12} \text{ sec}^{-1}$ ?

- a.  $3.7 \times 10^{-6} \text{ kg}$   
b.  $51 \times 10^{-3} \text{ kg}$   
c.  $1.96 \times 10^{-4} \text{ kg}$   
d.  $1.7 \times 10^{-6} \text{ kg}$

84. Half life period of the radioactive element X is 10 hours. Amount of X left of 11 the hour starting with one mol X is

- a.  $(1/2)^{1/10}$       b.  $(1/2)^{11/10}$   
c.  $(1/2)^{12/11}$       d.  $(1/2)^{1/11}$

85. A radioactive element 'A' decays by the sequence and with half lives, given below:



Which of the following statements is correct?

- a. B and C are isotopes  
b. The mass number of B is greater than A.  
c. Atomic number of A and C are same  
d. Disintegration constant  $k_2 > k_1$

86. A sample of radioactive substance gave 630 counts per minute and 610 counts per minute at times differing by 1 hour. The decay constant ( $\lambda$ ) in  $\text{min}^{-1}$  is given by

a.  $\lambda = \frac{630}{610} \times 60$

b.  $e^{60\lambda} = \frac{630}{610}$

c.  $\lambda = \frac{2.303}{60} \log \frac{610}{630}$

d.  $\lambda = \frac{2.303}{60} \times \frac{630}{610}$

87. In one type of mutual annihilation of an electron and a positron, three  $\gamma$ -ray photons are produced. If each photon has an energy of 0.3407 MeV, what is the mass of the positron in a.m.u? (1 amu = 931.5 MeV)

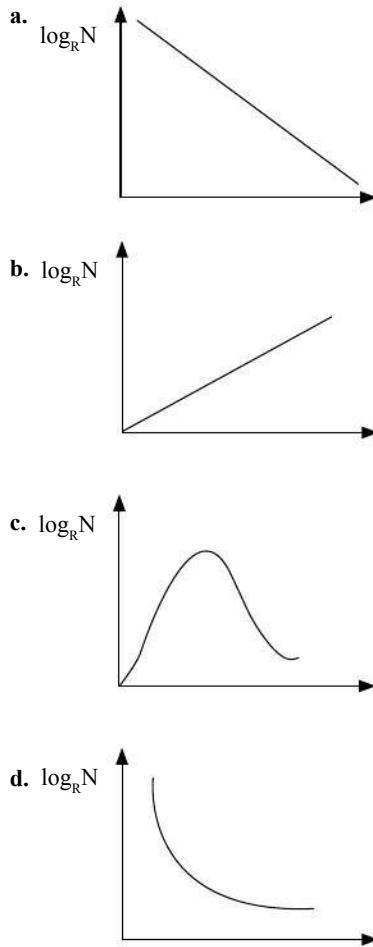
- a.  $7.986 \times 10^{-4}$       b.  $5.486 \times 10^{-4}$   
c.  $16.86 \times 10^{-4}$       d.  $2.243 \times 10^{-4}$

88. Assuming the age of the earth to be  $10^{10}$  years, what fraction of original amount of  $_{92}\text{U}^{238}$  is still in existence on earth ( $t_{1/2}$  of  $_{92}\text{U}^{238} = 4.51 \times 10^9$  years)?

- a. 10 %      b. 20 %  
c. 30 %      d. 40 %

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89. In the nuclear reaction:  ${}^3\text{Li}^7 + {}^1\text{H}^1 \rightarrow 2 {}_2\text{He}^4$  the mass loss is nearly 0.02 amu. Hence the energy released (in units of million kcal/mol) in the process is approximately
- 100
  - 200
  - 400
  - 600
90.  ${}_{90}\text{Th}^{232}$  decays to  ${}_{82}\text{Pb}^{206}$ . How many  $\alpha$ - and  $\beta$ -particles are emitted?
- $7\alpha, 6\beta$
  - $6\alpha, 7\beta$
  - $4\alpha, 3\beta$
  - none of these
91.  ${}_{92}\text{U}^{235} + {}_0\text{n}^1 \rightarrow {}_{92}\text{U}^{236} \rightarrow$  fission products + neutrons  
 $+ 3.20 \times 10^{-11} \text{ J}$
- The energy released when 1 g of  ${}_{92}\text{U}^{235}$  finally undergoes fission is
- $12.75 \times 10^8 \text{ kJ}$
  - $16.40 \times 10^7 \text{ kJ}$
  - $8.20 \times 10^7 \text{ kJ}$
  - $6.50 \times 10^6 \text{ kJ}$
92. During the transformation of  ${}^b\text{X}_a \rightarrow {}^d\text{Y}_c$  the number of  $\beta$ -particles emitted is
- $\frac{(b-d)}{4}$
  - $(c-a) + \frac{1}{2}(b-d)$
  - $(a-c) - \frac{1}{2}(b-d)$
  - $(b-d) + 2(c-a)$
  - $(b-d) + \frac{1}{2}(c-a)$
93. A sample of  $\text{U}^{238}$  ( $t_{1/2} = 4.5 \times 10^9$  yrs) ore is found to contain 23.8 g  $\text{U}^{238}$  and 20.6 g of  $\text{Pb}^{206}$ . Calculate the age of the ore.
- $4.9 \times 10^9$  year
  - $9.0 \times 10^{11}$  year
  - $9.4 \times 10^9$  year
  - $4.5 \times 10^9$  year
94. One of the hazards of nuclear explosion is the generation of  $\text{Sr}^{90}$  and its subsequent incorporation in bones. This nuclide has a half life of 28.1 years. Suppose one microgram was absorbed by a new born child, how much  $\text{Sr}^{90}$  will remain in his bones after 20 years?
- 61  $\mu\text{g}$
  - 61 g
  - 0.61  $\mu\text{g}$
  - none
95. The  $\log_e N$ - $\log_e t$  curve for radioactivity material is



96. One gram atom of an  $\alpha$ -emitting nuclide  ${}_z\text{X}^A$  (half life = 10 hours) was placed in a sealed container.  $4.52 \times 10^{23}$  He atoms will accumulate in the container in
- 9.40 hrs
  - 4.52 hrs
  - 20.00 hrs
  - 10.00 hrs
97. The radionuclieide  ${}_{90}\text{Th}^{234}$  undergoes two successive  $\beta$ -decays followed by one  $\alpha$ -decay. The atomic number and the mass number respectively of the resulting radio nuclieide are
- 92 and 234
  - 94 and 230
  - 90 and 230
  - 92 and 230
98. Consider the radioactive equilibrium sequence:
- $$\text{Ra}-226 \xrightarrow{\frac{\alpha}{1622 \text{ yrs}}} \text{Rn}-222 \xrightarrow{\frac{\alpha}{3.85 \text{ days}}} \text{Po}-218 \xrightarrow{\frac{\alpha}{3.05 \text{ mins}}} \text{Pb}-214 \longrightarrow \dots$$
- What is the number ratio of nuclides  $[\text{N}_{\text{Rn}-222}/\text{N}_{\text{Ra}-226}]$  under equilibrium?

- a.  $6.498 \times 10^{-6}$       b.  $6.645 \times 10^{-6}$   
 c.  $3.249 \times 10^{-6}$       d.  $6.102 \times 10^{-6}$
99. The half life of a radio isotope is four hours. If the initial mass of the isotope was 200 g the mass remaining after 24 hours undecayed is  
 a. 2.084 g      b. 3.125 g  
 c. 4.167 g      d. 1.042 g
100. A radioactive element gets spilled over the floor of a room. Its half life period is 30 days. If the initial activity is ten times the permissible value, after how many days will it be safe to enter the room?  
 a. 300 days      b. 10 days  
 c. 100 days      d. 1000 days

### Multiple Correct Answer Type Questions

101. Which one of the following processes result in transmutation to another element?  
 a. Electron capture  
 b. Alpha emission  
 c. Beta emission  
 d. Gamma emission
102. Which is/are correct about nuclear reactor?  
 a. Control rods : Cadmium and Beryllium  
 b. Coolent : Heavy water and Graphite  
 c. Moderator : Sodium metal  
 d. Reactor based on fusion is not possible
103. Which of the following statement is/are correct?  
 a. The decay constant is independent of external factors like temperature and pressure  
 b. Nuclear isomers have same number of protons and neutrons  
 c. The decay constant is independent of the amount of the substance used  
 d. The value of decay constant generally decreases with the rise in temperature
104. Which among these is/are correctly matched?  
 a. Positron emission : n/p ration increases  
 b. K - electron capture : n/p decreases  
 c.  $\beta^-$  decay : n/p ration decreases  
 d.  $\alpha$  - decay : n/p ratio increases

105. Select the correct statements:  
 a. In the reaction  $^{11}_{11}\text{Na} + Q \rightarrow ^{12}_{12}\text{Mg} + ^1_0\text{n}$ , the bombarding particle q is deuteron  
 b. In the reaction  $^{92}_{92}\text{U} + ^1_0\text{n} \rightarrow ^{56}_{36}\text{Ba} + ^{140}_{36}\text{Kr} + ^1_0\text{n}$ , produced p is  $^{36}_{36}\text{Kr}$   
 c. In a fission reaction, a loss in mass occurs releasing a huge amount of energy  
 d. A huge amount of energy is produced during nuclear fission and nuclear fusion reaction
106. Which statement/s about nuclear reactions is /are not true?  
 a. The rate of nuclear reaction is affected by catalysts.  
 b. Tremendous amounts of energy are involved in nuclear reactions.  
 c. New elements are never produced in a nuclear reaction.  
 d. Nuclear reaction involve valance electrons.
107. Which of the following pairs are isodioapheric pairs?  
 a.  $^{29}_{29}\text{Cu}^{65}$  and  $^{24}_{24}\text{Cr}^{55}$   
 b.  $^{29}_{29}\text{Cu}^{65}$  and  $^{24}_{24}\text{Cr}^{52}$   
 c.  $^{92}_{92}\text{U}^{235}$  and  $^{90}_{90}\text{Th}^{231}$   
 d.  $^{92}_{92}\text{U}^{238}$  and  $^{90}_{90}\text{Th}^{231}$
108. Which of the following statement is/are incorrect?  
 a. the end nuclide formed in thorium (4n) series is  $^{83}_{83}\text{Bi}^{200}$ .  
 b.  $^7_7\text{N}^{15}$  and  $^8_8\text{O}^{16}$  are isobars.  
 c.  $^{20}_{20}\text{Ca}^{40}$  has magic number of protons and magic number of neutrons  
 d. The radius (R) of a nuclide of mass number A is given by the equation  $R = R_0 (A)^{1/2}$  ( $R_0 = \text{constant}$ )
109. Which of the following statements is/are correct when balancing a nuclear equation?  
 a. The mass numbers must be conserved on both sides of the reaction arrow.  
 b. The ionic charges must be conversed on both sides of the reaction arrow.

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- c. The atomic numbers must be conserved on both sides of the reaction arrow.
- d. The elements must be the same on both sides of the reaction arrow.
110. Which of the following statement is/are incorrect?
- the end nuclide formed in thorium (4n) series is  $^{83}_{83}\text{Bi}^{200}$ .
  - $^7\text{N}^{15}$  and  $^8\text{O}^{16}$  are isobars.
  - $^{20}_{20}\text{Ca}^{40}$  has magic number of protons and magic number of neutrons
  - The radius ( $R$ ) of a nuclide of mass number  $A$  is given by the equation  $R = R_0 (A)^{1/2}$  ( $R_0$  =constant)
111. In the decay process
- $$\begin{array}{ccccccc} -\alpha & & -\beta & & -\beta \\ \text{P} & \rightarrow & \text{Q} & \rightarrow & \text{R} & \rightarrow & \text{S} \end{array}$$
- P and R are isotones
  - Q, R and S are isobars
  - P and S are isotopes
  - P and Q are isobars
112. Which of the following statement about gamma radiation is/are true?
- The mass number decreases by one with each gamma emitted.
  - Gamma rays are high energy photons.
  - It almost always accompanies alpha or beta emission.
  - It is a mechanism to release excess energy in the nucleus.
113. Unstable substances exhibit higher radioactivity due to
- high p/n ratio
  - low p/n ratio
  - $\text{p}/\text{n} = 1$
  - Both (a) and (b)
114. Which of the following particles can be accelerated in a cyclotron?
- Proton
  - Neutron
  - Alpha
  - Positron
115. Which is/are correct about the properties of rays?
- Effect on photographic film : $\alpha > \beta > \lambda$ .
  - Velocity :  $\alpha < \beta < \lambda$ .
  - Penetration power : $\alpha < \beta < \lambda$ .
  - Ionizing power : $\alpha > \beta > \lambda$ .
116. Which one of the following statements about isotopes is/are true?
- All isotopes beyond  $^{209}\text{Bi}$  are radioactive
  - Non radioactive isotopes generally have an odd number of neutrons
  - The ratio of neutrons to protons is about 1:1 for elements lighter than Ca.
  - The ratio of neutrons to protons is greater than 1:1 for elements heavier than Ca.
117. Which of the following equation is/ are correct?
- $^{55}\text{Cs}^{128} \rightarrow ^{56}\text{Ba}^{128} + \text{e}^-$
  - $^{53}\text{I}^{128} \rightarrow ^{52}\text{Te}^{128} + \text{e}^+$
  - $^{55}\text{Cs}^{128} \rightarrow ^{54}\text{Xe}^{128} + \text{e}^+$
  - $^{53}\text{I}^{128} \rightarrow ^{54}\text{Xe}^{128} + \text{e}^-$
118. Which of the following statement about electron capture is/are true?
- An outer shell valence electron is used
  - The electron is used to convert a proton to a neutron
  - In electron capture decay, the mass number remains unchanged.
  - In electron capture decay, the atomic number decreases by one.
119. Which relation is/are correct?
- 1 Ci =  $3.7 \times 10^{10}$  Bq
  - 1 Ci =  $2.8 \times 10^4$  Rd
  - 1 Bq = 1 dps.
  - 1 Bq =  $10^6$  Rd
120. Which of the following statements is/are incorrect, when the nuclide,  $^{19}\text{K}^{40}$ , is subject to K-electron capture?
- $^{40}\text{Ar}$  is produced with emission of  $\beta$ -particle.
  - $^{40}\text{Ar}$  is produced with emission of  $\alpha$  –particles.
  - $^{40}\text{Ar}$  is produced without emission of radiation
  - $^{40}\text{Ar}$  is produced with emission of X-radiation.

## Linked-Comprehension Type Questions

### Comprehension 1

The n /p ratio is an important factor for determining nuclear stability. By comparing a nuclide's n /p ratio with those in the band of stability, we can predict the mode of radioactive decay. In general, neutron -rich nuclei tend to emit beta particles; proton -rich nuclei tend to either emit positrons or undergo electron capture; heavy nuclei tend to emit alpha particles. The presence of magic numbers of nucleons and an even number of proton and neutrons are also important in determining the stability of a nucleus.

121. An unstable nucleus is characterized by

- (i) n /p > 1
  - (ii) low binding energy
  - (iii) high temperature and pressure
  - (iv) high packing fraction
- |                            |                                  |
|----------------------------|----------------------------------|
| <b>a.</b> (i), (ii)        | <b>b.</b> (i), (ii) (iv)         |
| <b>c.</b> (i), (ii), (iii) | <b>d.</b> (i), (ii), (iii), (iv) |

122. Which of the following nuclei are unstable?

- |                               |                              |
|-------------------------------|------------------------------|
| (i) ${}^8_4\text{Be}$         | (ii) ${}^{60}_{28}\text{Ni}$ |
| (iii) ${}^{56}_{26}\text{Fe}$ | (iv) ${}^{14}_6\text{C}$     |
- |                       |                      |
|-----------------------|----------------------|
| <b>a.</b> (i), (iv)   | <b>b.</b> (i), (ii)  |
| <b>c.</b> (iii), (iv) | <b>d.</b> (ii), (iv) |

123. The mode of decay of P-28 and P-34 is respectively
- a. By  $\beta$  emission or K electron capture and positron emission
  - b. By positron emission and K electron capture
  - c. By positron emission or K electron capture and  $\beta$  emission
  - d. By K electron capture in both the cases

### Comprehension 2

Radioactive decay is kinetically a first order process hence the decay rate or reactivity is proportional to the number of radioactive nuclei (N) as follows

$$\text{Decay rate} = \lambda \times N$$

The integrated form for a first order rate law can be given as

$$\ln \left( \frac{N}{N_0} \right) = -\lambda t$$

Radio nuclides consequently have constant half lives which is independent of mass of the nuclide and external factors.

124. How much time is required for a 5.75 -mg sample of  ${}^{51}\text{Cr}$  to decay to 1.50 mg if it has a half-life of 27.8 days?

- |                     |                     |
|---------------------|---------------------|
| <b>a.</b> 5.39 days | <b>b.</b> 2.69 days |
| <b>c.</b> 53.9 days | <b>d.</b> 5.49 days |

125. Potassium-40 decays to argon-40 with a half life of  $1.27 \times 10^9$  yr. What is the age of a rock in which the mass ratio of  ${}^{40}\text{Ar}$  to  ${}^{40}\text{K}$  is 3.6?

- |                                   |                                |
|-----------------------------------|--------------------------------|
| <b>a.</b> $2.8 \times 10^{10}$ yr | <b>b.</b> $1.4 \times 10^9$ yr |
| <b>c.</b> $1.4 \times 10^{10}$ yr | <b>d.</b> $2.8 \times 10^9$ yr |

126. Polonium -210, with a half life of 138 days, decay by alpha emission to stable lead-206. The alpha particles so emitted, one they lose their energy, pick up electrons from their surrounding and becomes helium atoms. Suppose the He gas originating from all of the alpha particles is collected. What volume of He gas, in liters, at 25°C and 0.800 atm pressure, would be obtained from a 5.00 g sample of polonium-10 left to decay for 138 days?

- |                   |                   |
|-------------------|-------------------|
| <b>a.</b> 3.64 L  | <b>b.</b> 0.364 L |
| <b>c.</b> 0.182 L | <b>d.</b> 1.82 L  |

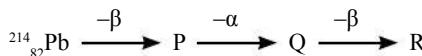
### Comprehension 3

A nuclide may undergo a series of decay steps before stable nuclei forms. This series of steps is called a radioactive series or a nuclear disintegration series. There are four series out of which only one (Neptunium) series is artificial.

127. A radioactive decay series that begins with  ${}^{237}_{93}\text{Np}$  ends with formation of the stable nuclide  ${}^{209}_{82}\text{Bi}$ . How many alpha-particle emissions and how many beta-particle emissions are involved in the sequence of radioactive decays?

- |                                  |                                  |
|----------------------------------|----------------------------------|
| <b>a.</b> 6 $\alpha$ , 4 $\beta$ | <b>b.</b> 7 $\alpha$ , 2 $\beta$ |
| <b>c.</b> 8 $\alpha$ , 6 $\beta$ | <b>d.</b> 7 $\alpha$ , 4 $\beta$ |

128. Consider the nuclear change reaction given below and select the correct statements.



- (i) P is an isobar of Pb - 214

- (ii) Q and R isobars

- (iii) Q is an isotope of Pb- 214

- (iv) R is an isotope of Pb -214

- |                                  |  |
|----------------------------------|--|
| <b>a.</b> (i), (ii)              |  |
| <b>b.</b> (i), (ii), (iv)        |  |
| <b>c.</b> (ii), (iii), (iv)      |  |
| <b>d.</b> (i), (ii), (iii), (iv) |  |

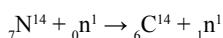
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129. Which of the following is not correctly matched?

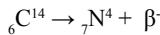
- (i)  $_{86}^{220}\text{Rn}$  : 4n - series
  - (ii)  $_{88}^{226}\text{Ra}$  : 4n - series
  - (iii)  $_{89}^{225}\text{Ac}$  : 4n + 1 - series
  - (iv)  $_{91}^{231}\text{Pa}$  : 4n + 1 - series
- a. (ii), (iv)   b. (ii),(iii)  
c. (iii), (iv)   d. (i), (iv)

### Comprehension 4

C – 14 is used to determine the age of organic material. The procedure is based on the formation of  $^{14}\text{C}$  by neutron capture in the upper atmosphere.



$^{14}\text{C}$  is absorbed by living organisms during photosynthesis. The  $^{14}\text{C}$  content is constant in living organism once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of  $^{14}\text{C}$  in the dead being falls due to the decay which  $^{14}\text{C}$  undergoes



The half life period of  $^{14}\text{C}$  is 5770. The decay constant ( $\lambda$ ) can be calculated by using the following formula  $\lambda = 0.693 / t \frac{1}{2}$ .

The comparison of the  $\beta^-$  activity of the dead matter with that of the carbon still in circulation enables measurement of the period of the isolation of the material from the living cycle. The method however, ceases to be accurate over periods longer than 30,000 years. The proportion of  $^{14}\text{C}$  to  $^{12}\text{C}$  in living matter is  $1 : 10^{12}$ .

130. Which of the following option is correct?

- a. In living organisms, circulation of  $^{14}\text{C}$  from atmosphere is high so the carbon content is constant in organism.
- b. carbon dating can be used to find out the age of earth crust and rocks
- c. radioactive absorption due to cosmic radiation is equal to the rate of radioactive decay, hence the carbon content remains constant in living organism
- d. carbon dating cannot be used to determine concentration of  $^{14}\text{C}$  in dead beings.

[IIT 2006]

131. What should be the age of fossil for meaningful determination of its age?

- a. 6 years
- b. 6000 years

c. 60,000 years

d. it can be used to calculate any age

[IIT 2006]

132. Nuclear explosion has taken place leading to increase in concentration of  $^{14}\text{C}$  in nearby areas.  $^{14}\text{C}$  concentration is  $C_1$  in nearby areas and  $C_2$  in areas far away. If the age of the fossil is determined to be  $T_1$  and  $T_2$  at the places respectively then

- a. The age of the fossil will increase at the place where explosion has taken place and

$$T_1 - T_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$$

- b. The age of the fossil will decrease at the place where explosion has taken place and

$$T_1 - T_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$$

- c. The age of fossil will be determined to be same

$$d. T_1 / T_2 = C_1 / C_2$$

[IIT 2006]

### Assertion-Reason Type Questions

In the following questions, two statements (Assertion) A and Reason (R) are given. Mark

- (a) if A and R both are correct and R is the correct explanation of A.
- (b) if A and R both are correct but R is not the correct explanation of A.
- (c) A is true but R is false.
- (d) A is false but R is true.

133. (A): The neutrons are better initiators of nuclear reaction, than the protons, neutrons of  $\alpha$  - particles of the same energy.

(R): Neutrons are uncharged particles and hence, they are not repelled by positively charged nucleus.

134. (A):  $\beta$ -particles are emitted by nucleus.

(R): In nucleus,  ${}_0\text{n}^1 \rightarrow {}_1\text{p}^1 + {}_{-1}\text{e}^0$ .

135. (A): Nucleide  $_{13}^{30}\text{Al}$  is less stable than  $_{20}^{40}\text{Ca}$ .

(R): Nucleide having odd number of protons and neutrons are generally unstable.

136. (A): The activity of 1 g of uranium-235 will be greater than the same amount present as  $\text{U}_3\text{O}_8$ .

(R): In combined state, the amount of uranium is less.

- 137.** (A): To separate U-235 from the more abundant, all the uranium converted into  $\text{UF}_6$ .  
 (R):  $\text{UF}_6$  is one of the few compounds that exist in gaseous state under ordinary conditions which helps in separation of U-235 from U-238.
- 138.** (A): 500 mg of an isotope becomes 250 mg in 120 minute. Therefore 100 mg of the isotope will become 50 mg in 24 minutes.  
 (R): The process of radioactive decay follows first-order kinetics.
- 139.** (A): Due to K-electron capture n/p ratio increases.  
 (R): K electron capture increases one neutron though number of protons remains the same.
- 140.** (A): The average life of a radioactive element is infinity.  
 (R): As a radioactive element disintegrates, more of it is formed in the nature by itself.
- 141.** (A): The reactions taking place in the sun are nuclear fusion reactions.  
 (R): The main reason for nuclear fusion reactions in the sun is that  $\text{H}_2$  is present in the sun's atmosphere so that hydrogen nuclei can fuse to form helium.
- 142.** (A): Nuclide  ${}_{13}\text{Al}^{30}$  is less stable than  ${}_{20}\text{Ca}^{40}$ .  
 (R): Nuclides having odd number of protons and neutrons are generally unstable.
- 143.** (A): Artificial nuclear reactions are carried out by charged particles.  
 (R): Charged particles cannot be accelerated.
- 144.** (A): The activation energies for fusion reactions are very low.  
 (R): They require very high temperature to overcome electrostatic repulsion between the nuclei.
- 145.** (A): The archeological studies are based on the radioactive decay of carbon-14 isotope.  
 (R): The ratio of C-14 to C-12 in the animals and plants is same as that in the atmosphere.
- 146.** (A): Mass number of an atom is equal to total number of nucleons present in the nucleus.  
 (R): Mass number defines the identity of an atom.
- 147.** (A): For maximum stability N/P ratio must be equal to 1.  
 (R): Loss of  $\alpha$ - and  $\beta$ -particles has no role in N/P ratio.

- 148.** (A): It is not possible to use  ${}^{35}\text{Cl}$  as fuel for fusion energy.  
 (R) The binding energy  ${}^{35}\text{Cl}$  is too small
- 149.** (A):  ${}_{92}\text{U}^{235} + {}_0\text{n}^1 \rightarrow {}_{56}\text{Ba}^{140} + {}_{36}\text{Kr}^{93} + {}_3 {}_0\text{n}^1$  is a nuclear fission reaction.  
 (R): Neutrons emitted can not react further to cause reaction.

### Matrix-Match Type Questions

**150.** Match the lists I and II and pick the correct matching from the codes given below.

**List I**      **List II**

- |              |                                                                                                       |
|--------------|-------------------------------------------------------------------------------------------------------|
| A. Isotope   | (p) ${}_{88}\text{Ra}^{228}$ and ${}_{89}\text{Ac}^{228}$                                             |
| B. Isobar(q) | (q) ${}_{18}\text{Ar}^{39}$ and ${}_{19}\text{K}^{40}$                                                |
| C. Isotone   | (r) ${}_1\text{H}^2$ and ${}_1\text{H}^3$                                                             |
| D. Isosters  | (s) ${}_{92}\text{U}^{235}$ and ${}_{92}\text{U}^{238}$<br>(t) $\text{CO}_2$ and $\text{N}_2\text{O}$ |

**151.** Match the following:

**List I**      **List II**

- |                                 |                                |
|---------------------------------|--------------------------------|
| A. ${}_{20}\text{Ca}^{40}$ (p)  | unstable, alpha emitter        |
| B. ${}_{53}\text{I}^{133}$      | (q) unstable, beta emitter     |
| C. ${}_{53}\text{I}^{121}$      | (r) unstable, positron emitter |
| D. ${}_{90}\text{Th}^{232}$ (s) | stable                         |

**152.** Match the following:

**List I**      **List II**

- |                                                                               |                                 |
|-------------------------------------------------------------------------------|---------------------------------|
| A. ${}_0\text{n}^1 \rightarrow {}_1\text{p}^1 + {}_{-1}\text{e}^0 + \text{V}$ | (p) Beta emission               |
| B. ${}_1\text{p}^1 \rightarrow {}_0\text{n}^1 + {}_1\text{e}^0 + \text{V}$    | (q) Positron                    |
| C. ${}_1\text{p}^1 + {}_{-1}\text{e}^0 \rightarrow {}_0\text{n}^1 + \text{V}$ | (r) Proton emission             |
| D. Emission by nuclei in very high energy state                               | (s) K-electron capture (-8 MeV) |

**153.** Match the following:

**List I**      **List II**

- |             |                                                      |
|-------------|------------------------------------------------------|
| A. Isotones | (p) ${}_{20}\text{Ca}^{40}$ , ${}_{19}\text{K}^{40}$ |
| B. Isotopes | (q) ${}_{14}\text{Si}^{30}$ , ${}_{15}\text{P}^{31}$ |

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- C. Isobars (r)  ${}_{9}^{19}\text{F}$ ,  ${}_{11}^{23}\text{Na}$   
 D. Isodiaphers (s)  ${}_{17}^{35}\text{Cl}$ ,  ${}_{17}^{37}\text{Cl}$   
 (t)  ${}_{7}^{15}\text{N}$ ,  ${}_{8}^{16}\text{O}$

154. Match the following:

List I	List II
A. end product of $(4n + 1)$ series	(p) ${}_{94}^{241}\text{Pu}$
B. starting product of uranium series	(q) ${}_{83}^{209}\text{Bi}$
C. starting product of $4n$ series	(r) ${}_{90}^{232}\text{Th}$
D. starting product of artificial radioactive series	(s) ${}_{92}^{238}\text{U}$
	(t) ${}_{88}^{226}\text{Ra}$

155. Match the following:

List I (Series)	List II
A. Thorium series	(p) $8\alpha, 5\beta$
B. Naptunium series	(q) $8\alpha, 6\beta$
C. Actinium series	(r) $6\alpha, 4\beta$
D. Uranium series	(s) $7\alpha, 4\beta$
	(t) Natural series

156. Match the following:

List I (Reactions)	List II (Particles)
A. ${}_{4}^{9}\text{Be} + {}_{2}^{4}\text{He} \rightarrow {}_{6}^{12}\text{C} + \dots$	(p) ${}_{2}^{4}\text{He}$
B. ${}_{6}^{12}\text{C} + \dots \rightarrow {}_{5}^{10}\text{B} + {}_{2}^{4}\text{He}$	(q) ${}_{0}^{1}\text{n}$
C. ${}_{7}^{14}\text{N} + \dots \rightarrow {}_{8}^{17}\text{O} + {}_{1}^{1}\text{H}$	(r) ${}_{1}^{2}\text{D}$
D. ${}_{20}^{40}\text{Ca} + \dots \rightarrow {}_{19}^{37}\text{K} + {}_{2}^{4}\text{He}$	(s) ${}_{1}^{1}\text{H}$

157. Match the following:

List I	List I
A. $\text{P}^{32}$	(p) Location of tumor in the brain
B. $\text{Na}^{24}$	(q) Location of blood clots and circulatory disorders
C. $\text{Co}^{60}$	(r) Radiotherapy

- D.  $\text{I}^{131}$  (s) Agricultural research  
 (t) In the treatment of thyroid gland

$\text{P}^{32}$  is used in agricultural research.  $\text{Na}^{24}$  is used in location of blood clots and circulatory disorders.  $\text{Co}^{60}$  is used in radiotherapy.  $\text{I}^{131}$  is used in location of tumour in the brain.

158. Match the following:

List I	List II
A. $\alpha$ - particle emission	(p) Increases n / p ratio
B. $\beta$ - particle emission	(q) Decreases n / p ratio
C. K electron capture	(r) Atomic no. decreases by one unit
D. Positron emission	(s) Atomic no. decreases by two units
	(t) Atomic no. increases by one unit

159. Match the following:

List I	List II
A. Nuclear fission	(p) Combination of lighter nuclei
B. Nuclear fussion	(q) Splitting of heavy nuclei into lighter ones
C. Spallation reaction	(r) Possible by high energy bombarding particles
D. Chemical reactions	(s) Possible by valence electron
	(t) Thermo nuclear reaction needing

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160. Loss of a  $\beta$ -particle is equivalent to  
 a. increase of one proton only  
 b. decrease of one neutron only

- c. both **a** and **b**
  - d. none of these

[IIT 1998]

161. Decrease in atomic number is observed during

  - (1)  $\alpha$  – emission
  - (2)  $\beta$  – emission
  - (3) positron emission
  - (4) electron capture

select the correct answer

- a. 1,2,3      b. 2,3,4  
c. 1,3,4      d. 1,2,3,4

[IIT 1998]



[HT 1999]

- 163**  $^{92}_{\text{U}}\text{U}^{238}$  is radioactive and it emits  $\alpha$  and  $\beta$ -particles to form  $^{82}_{\text{Pb}}\text{Pb}^{206}$ . The number of  $\alpha$  and  $\beta$ -particles are respectively

- a.** 8, 6      **b.** 6, 8  
**c.** 4, 2      **d.** 8, 4

[HT 2000]

- 164.**  $\text{Na}^{23}$  is the more stable isotope of Na. Find out the process by which  ${}_{11}\text{Na}^{24}$  can undergo radioactive decay

- a.  $\beta$  emission
  - b.  $\alpha$  emission
  - c.  $\beta^+$  emission
  - d. K electron capture

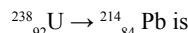
[IIT 2003]

- 165.** A positron is emitted from  $_{11}^{23}\text{Na}$ . The ratio of the atomic mass and atomic number of the resulting nuclide is

- a.  $22 / 10$       b.  $22 / 11$   
c.  $23 / 10$       d.  $23 / 12$

[IIT 2007]

- 166.** The total number of  $\alpha$  and  $\beta$  particles emitted in the nuclear reaction



[IIT 2009]



## ANSWERS

## Straight Objective Type Questions

- 1.** a    **2.** b    **3.** d    **4.** b    **5.** b    **6.** b    **7.** c    **8.** d    **9.** b    **10.** b    **11.** c    **12.** c  
**13.** c    **14.** c    **15.** d    **16.** b    **17.** d    **18.** a    **19.** b    **20.** c    **21.** c    **22.** c    **23.** c    **24.** b  
**25.** d    **26.** a    **27.** b    **28.** d    **29.** a    **30.** c    **31.** d    **32.** a    **33.** b    **34.** c    **35.** a    **36.** a  
**37.** a    **38.** b    **39.** a    **40.** c    **41.** a    **42.** a    **43.** a    **44.** d    **45.** a    **46.** c    **47.** c    **48.** d  
**49.** c    **50.** b

## Brainteasers Objective Type Questions

- 51.** a    **52.** d    **53.** d    **54.** b    **55.** b    **56.** b    **57.** c    **58.** c    **59.** c    **60.** a    **61.** c    **62.** b  
**63.** a    **64.** b    **65.** c    **66.** c    **67.** b    **68.** c    **69.** b    **70.** b    **71.** b    **72.** b    **73.** d    **74.** b  
**75.** d    **76.** c    **77.** a    **78.** b    **79.** a    **80.** c    **81.** b    **82.** a    **83.** c    **84.** b    **85.** c    **86.** b  
**87.** b    **88.** b    **89.** c    **90.** a    **91.** c    **92.** b    **93.** d    **94.** c    **95.** a    **96.** c    **97.** c    **98.** a  
**99.** b    **100.** c

**Multiple Correct Answer Type Questions**

- 101.** a, b, c    **102.** b, c, d    **103.** a, b, c    **104.** a, c, d    **105.** b, c, d    **106.** a, c, d    **107.** a, c  
**108.** a, b, d    **109.** a, c    **110.** a, b, d    **111.** b, c    **112.** b, c, d    **113.** d    **114.** a, c, d  
**115.** b, c, d    **116.** a, c, d    **117.** b, c, d    **118.** b, c, d    **119.** a, c, d    **120.** a, b, c

**Linked-Comprehension Type Questions****Comprehension 1**

- 121.** b    **122.** a    **123.** c

**Comprehension 2**

- 124.** c    **125.** d    **126.** b

**Comprehension 3**

- 127.** d    **128.** b    **129.** a

**Comprehension 4**

- 130.** c    **131.** b    **132.** a

**Assertion Reason Answers**

- |               |               |               |               |
|---------------|---------------|---------------|---------------|
| <b>133.</b> a | <b>134.</b> a | <b>135.</b> a | <b>136.</b> a |
| <b>137.</b> a | <b>138.</b> d | <b>139.</b> c | <b>140.</b> c |
| <b>141.</b> b | <b>142.</b> a | <b>143.</b> c | <b>144.</b> d |
| <b>145.</b> c | <b>146.</b> c | <b>147.</b> c | <b>148.</b> c |
| <b>149.</b> c | <b>150.</b> c |               |               |

**Matrix-Match Type Questions**

- 151.** A - (r, s), B - (p), C - (q), D - (t)  
**152.** A - (s), B - (q), C - (r), D - (p)  
**153.** A - (p), B - (q), C - (r), D - (s)  
**154.** A - (q, t), B - (s), C - (p), D - (r)  
**155.** A - (q), B - (s, t), C - (r), D - (p)  
**156.** A - (r, t), B - (p), C - (s, t), D - (q, t)  
**157.** A - (q), B - (r), C - (p), D - (s)  
**158.** A - (s), B - (q), C - (r), D - (p, t)  
**159.** A - (p, s), B - (q, t), C - (p, r), D - (p, r)  
**160.** A - (q), B - (p, t), C - (r), D - (s)

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- 161.** c    **162.** c    **163.** d    **164.** a    **165.** a    **166.** c

**Hints and Explanations****Straight Objective Type Questions**

4. For  $^{82}_{\Lambda}\text{Pb}^{208}$ , number of protons = 82 and number of neutrons = 126, both of which are magic numbers.  
11. 
$${}^A_Z \text{X} \rightarrow {}^{A-1}_{Z+1} \text{Y} + {}^0_{-1} \text{e} + \nu$$
  
14. Since the mass number has decreased by 12 : 3  $\alpha$  emissions have occurred. The charge number will

decrease by 6 with 3  $\alpha$  emission. 4 $\beta$  emission will make charge 84 units.

22. It depends only on the number of nuclei present at that time  
24. For (15/16) disintegration;  
fraction remaining = 1/16.  
 $1/16 = (1/2)^4$

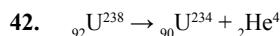
so time for (15 / 16) disintegration

$$= 4 \times 160 \text{ days} = 640 \text{ days.}$$

41.  $t_{av} = \frac{1}{\lambda} 100\text{s}$

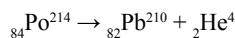
$$t_{1/2} = \frac{0.693}{\lambda}$$

$$= 69.3\text{s}$$

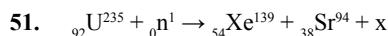


43.  ${}_{27}^{57}\text{Co}$  decays  ${}_{26}^{57}\text{Fe}$ . The mass  ${}_{26}^{57}\text{Fe}$  is 0.000897 v less than  ${}_{26}^{57}\text{Co}$  makes it suitable for electron capture.

48.  ${}_{84}\text{Po}^{214}$  has high atomic number, greater than 83 (which corresponds to the heavy stable nuclide,  ${}_{83}\text{Bi}^{209}$ )



### Brainteasers Objective Type Questions



$$92 + 0 = 54 + 38 + \text{a}$$

$$\text{a} = 0$$

$$235 + 1 = 139 + 94 + \text{b}$$

$$\text{b} = 3$$

$$\text{So } \text{x} = 3 {}_0\text{n}^1$$

52.  $Q = (M_R - M_p) C^2 = a + b - c$

54.  $10 \text{ mC} = 10 \times 10^{-3} \times 3.7 \times 10^{10}$

$$= 3.7 \times 10^8 = - \frac{dN}{dt} = \lambda N \text{ disint./sec.}$$

$$\lambda = 2.2 \times 10^{-12} \text{ s}^{-1}$$

Therefore

$$\lambda = \frac{3.7 \times 10^8}{2.2 \times 10^{-12}} = 1.68 \times 10^{20}$$

55. All natural radioactive decay processes are of first order. So (b) option is correct.

56. Rate of disintegration =  $dN/dt$

$$= 3.76 \times 10^{10} \text{ sec}^{-1}$$

number of atoms in the beginning

$$= \frac{1}{226} \times 6.02 \times 10^{23}$$

$$= 2.66 \times 10^{21}$$

Using the expression

$$- dN / dt = \lambda N_0$$

$$\lambda = \frac{3.76 \times 10^{10}}{2.66 \times 10^{21}} = 1.41 \times 10^{-11}$$

$$t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{1.41 \times 10^{-11}} \text{ sec}$$

$$= 4.9 \times 10^{10} \text{ sec}$$

59.  $N = N_0 (1/2)^n$

$$\text{Number of half lives (n)} = 12 \text{ days} / 3 \text{ days} = 4$$

$$N = 3 \text{ g}$$

$$3 \text{ g} = N_0 (1/2)^4 = N_0 / 16$$

$$N_0 = 3 \text{ g} \times 16 = 48 \text{ g}$$

60. Mass loss = Mass of [2p + 2n - He]

$$= 2 \times 1.0078 + 2 \times 2.0187 - 4.0026$$

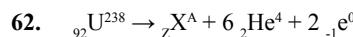
$$= 0.0304 \text{ amu}$$

$$= 0.0304 \times 931.5 = 28.72 \text{ MeV}$$

$$\text{So B.E. / nucleon} = 28.72 / 4 = 7.18 \text{ MeV}$$

61.  $Q = [24.990432 \text{ u} - 24.985839 \text{ u} - 2m_e]c^2$

$$= 0.004593(931.5) - 1.102 = 303 \text{ MeV}$$



From the conversion of charge and mass number, we get

$$92 = Z + 12 - 2$$

$$Z = 82$$

$$238 = A + 24 + 0$$

$$A = 214$$

Therefore the end product is  ${}_{82}\text{Pb}^{214}$ .

63.  $\lambda = \lambda_1 + \lambda_2$

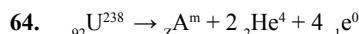
$$\lambda = \frac{0.693}{2.68} \text{ yr}^{-1}$$

$$\lambda_1 = \frac{0.693}{2.658} \times \frac{86}{100} = \frac{0.693}{T_{1/2}}$$

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$$\text{so } T_{1/2} = \frac{0.693 \times 2.68 \times 100}{0.693 \times 86} = \frac{268}{86}$$

$$= 3.11 \text{ years}$$



$$\text{thus } Z + 4 - 4 = 92$$

$$Z = 92$$

$$\text{and } m + 8 = 238$$

$$m = 238 - 8 = 230 \text{ i.e., } {}_{92}^{\text{U}}\text{U}^{238}$$

65.  $\lambda = \frac{0.693}{T_{1/2}} = 2.95 \times 10^{-8} \text{ s}^{-1}$

$$N_o = \frac{-dN/dt}{\lambda} = \frac{7.4 \times 10^{-4}}{2.95 \times 10^{-8}}$$

$$= 2.51 \times 10^{12} \text{ nuclei.}$$

$$N_{(t)} = N_o e^{-\lambda t} = 2.51 \times 10^{12} e^{-2.95 \times 10^{-8} \cdot 3.156 \times 10^7}$$

$$= 0.394 (2.51 \times 10^{12}).$$

$$\text{Activity} = \lambda N_{(t)} = 0.394 (2.5 \times 10^{12}) \times 2.95 \times 10^{-8}$$

$$= 0.788 \mu\text{Ci}$$

66.  $T = \frac{2.303 \times t_{1/2}}{0.693} \log_{10} \frac{N_0}{N}$

$$= \frac{2.303 \times 5760}{0.693} \log_{10} \frac{200}{25}$$

$$= 17280 \text{ years}$$

67.  $\lambda_{\text{eff}} = \lambda_1 + \lambda_2 \text{ or } \frac{1}{t_{\text{eff}}} = \frac{1}{t_1} + \frac{1}{t_2}$

69.  $530 = N_0 \cdot e^{-\lambda \cdot t_1}$

$$510 = N_0 \cdot e^{-\lambda \cdot t_2}$$

$$530 / 510 = e^{\lambda(t_2 - t_1)}$$

$$530 / 510 = e^{60\lambda}$$

$$\text{Here } (t_2 - t_1) = 60 \text{ mins.}$$

$$\text{Taking log, } 60\lambda = \ln 530 / 510$$

$$\text{i.e., } \lambda = \frac{1}{60} \ln \frac{530}{510}$$

or

$$\lambda = \frac{2.303}{60} \log \frac{530}{510}$$

73. Given  $t_{1/2} = 12.3 \text{ years}$

$$\text{Initial amount } (N_0) = 32 \text{ mg}$$

$$\text{Total time} = 49.2 \text{ years}$$

$$\text{Number of half lives (n)} = T / t_{1/2}$$

$$= 49.2 / 12.3 = 4$$

$$N_t = N_0 (\frac{1}{2})^n = 32 (\frac{1}{2})^4$$

$$= 32 / 16 = 2 \text{ mg}$$

75.  $N / N_0 = 1 / 16$

$$N_0 / N = 2^n$$

$$16 = 2^n$$

$$n = 4$$

$$4 \text{ half lives} = 192 \text{ min.}$$

$$1 \text{ half life} = 192 / 4 = 48 \text{ min.}$$

76.  $\frac{3}{2} kT = \frac{(2e)^2}{4\pi\epsilon_0 r}$

$$T = \frac{8 \times (1.6 \times 10^{-19})^2 \times 9 \times 10^9}{3 \times 1.38 \times 10^{-23} \times 2 \times 10^{-15}}$$

$$= 2.23 \times 10^{10} \text{ K}$$

77.  $t_{1/2} = 8 \text{ days}$

$$\text{number of half lives in 32 days}$$

$$n = 32 / 8 = 4$$

$$N_0 = N \cdot 2^n = (125 \text{ mg}) \cdot 2^4$$

$$= 125 \times 16 \text{ mg} = 200 \text{ mg} = 2 \text{ g}$$

78.  $18 \text{ hrs} = 6 \text{ half-lives}$

$$(1/2)^6 = \frac{3.125 \text{ g}}{m_0 \text{ g}}$$

Here  $m_0 \text{ g}$  is the initial mass.

$$\frac{1}{64} = \frac{3.125}{m_0}$$

$$m_0 = 200 \text{ g}$$

79.  ${}_a^c\text{C} \rightarrow {}_d^b\text{N} + m {}_2^4\text{He}^4 + n {}_{-1}^0\text{e}^0$

$$\text{So } c = b + 4m$$

$$\text{Hence } m = \frac{c - b}{4} \text{ and } a = d + 3m - n$$

$$\text{i.e., } n = d + 2m - a = d + [(c - b) / 2] - a$$

81.  $dN / dt = \lambda \cdot N$

$$1.18 \times 10^{13} = \frac{1}{T} \times \frac{1}{12} \times 6.023 \times 10^{23}$$

$$T = \frac{6.023 \times 10^{23}}{1.18 \times 10^{13} \times 12} \text{ minutes}$$

$$T = \frac{6.023 \times 10^{23}}{1.18 \times 10^{13} \times 12 \times 60 \times 24 \times 265} \cdot$$

$$= 8100 \text{ years.}$$

82.  $\frac{N_X}{N_Y} = \frac{k_Y}{k_X} = \frac{T_{50}(X)}{T_{50}(Y)}$

$$\frac{3.1 \times 10^9}{1} = \frac{2 \times 10^{10}}{T_{50}(Y)}$$

$$T_{50}(Y) = 6.45 \text{ years}$$

83. As 1 curie =  $3.7 \times 10^{10}$  dps

$$\text{Rate} = \lambda \cdot \frac{w}{14} \times N_0$$

$$3.7 \times 10^{10} = 4.4 \times 10^{-12} \times \frac{w}{14} \times 6.02 \times 10^{23}$$

On solving we get,

$$w = 1.96 \times 10^{-1} \text{ g} = 1.96 \times 10^{-4} \text{ kg}$$

84. X left after 10 hours = 0.5 mol

$$X \text{ left after 11 hours} =$$

$$\text{Using } N = N_0 (1/2)^n$$

$$\text{As } n = \frac{T}{t_{1/2}} = \frac{1}{10}.$$

$$N_0 = 1/2$$

$$\text{So } N = (1/2) (1/2)^{1/10} = (1/2)^{11/10}$$

$$\text{Here } n = T / t_{1/2} = 1/10 \text{ and}$$

$N_0$  = initial amount which is now  $(1/2)$  mol after 10 hours.

85. For A :  $t_{1/2} = 30 \text{ min}$

$$k_1 = \frac{0.693}{30} = 0.0231$$

$$\text{For B : } t_{1/2} = 2 \times 24 \times 60 \text{ min}$$

$$k_2 = \frac{0.693}{2 \times 24 \times 60} = 0.000240$$

$$\text{So } k_1 > k_2$$

Also emission of one one  $\alpha$  and two  $\beta$  gives rise to the formation of isotope, i.e., A and C have same atomic number.

86.  $630 = N_0 \cdot e^{-\lambda t_1}$

$$610 = N_0 \cdot e^{-\lambda t_2}$$

$$630 / 610 = e^{\lambda(t_2 - t_1)}$$

$$630 / 610 = e^{60\lambda}$$

$$\text{Here } (t_2 - t_1) = 60 \text{ mins.}$$

$$\text{Taking log, } 60\lambda = \ln 630 / 610$$

$$\text{i.e., } \lambda = \frac{1}{60} \ln \frac{630}{610}$$

or

$$\lambda = \frac{2.303}{60} \log \frac{630}{610}$$

87. Energy of three  $\gamma$ -ray photons

$$= 3 \times 0.3407 \text{ MeV} = 1.0021 \text{ MeV}$$

$$= \frac{1.0221}{931.5} \text{ a.m.u,}$$

which is the total mass of one electron and one positron.

Therefore the mass of one positron

$$= \frac{1.0221}{931.5 \times 2} = 5.486 \times 10^{-4} \text{ a.m.u}$$

88.  $t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N}$

$$\lambda = \frac{0.693}{4.51 \times 10^9} = 1.54 \times 10^{-10} \text{ year}^{-1}$$

$$10^{10} \text{ year} = \frac{2.303}{1.54 \times 10^{-10} \text{ year}^{-1}} \log_{10} \frac{N_0}{N}$$

$$\log_{10} \frac{N_0}{N} = \frac{10^{10} \times 1.54 \times 10^{-10}}{2.303} = 0.6687$$

$$\frac{N_0}{N} = 4.663$$

$$N / N_0 = 0.21445$$

Fraction of original amount of  $^{92}\text{U}^{238}$  left in the earth = 20 %

89. Mass loss per atom of He formed =  $0.02 / 2 = 0.01$  amu

## 11.38 ■ Nuclear Chemistry

Mass loss per mole of He =  $0.01 \times 6.02 \times 10^{23}$  amu/mol

as 1 amu =  $0.3537 \times 10^{-10}$  cal

So energy released

$$= 0.01 \times 6.02 \times 10^{23} \frac{\text{amu}}{\text{mol}}$$

$$\times \frac{0.3537 \times 10^{-10}}{1 \text{ amu}} \text{ cal}$$

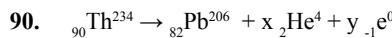
$$= 0.01 \times 6.02 \times 10^{23} \times 0.3537 \times 10^{-10} \times 10^{-9}$$

$$= 0.01 \times 6.02 \times 10^{23} \times 0.3537 \times 10^{-19}$$

M kcal/mol

$$= 212 \text{ M kcal/mol}$$

$$= 200 \text{ M kcal/mol}$$



compare mass number

$$234 = 206 + 4x$$

$$4x = 234 - 206 = 28$$

$$x = 28/4 = 7 \text{ (\alpha)}$$

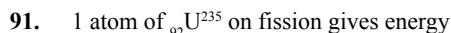
compare atomic number

$$90 = 82 + 2x - y$$

$$x = 7$$

$$90 = 82 + 14 - y$$

$$y = 96 - 90 = 6 \text{ (\beta)}$$



$$= 3.2 \times 10^{-11} \text{ J}$$

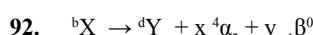
$6.023 \times 10^{23}$  atom (1 mole) on fission gives energy  
 $= 3.2 \times 10^{-11} \times 6.023 \times 10^{23} \text{ J}$

235 gm of  ${}_{92}^{\text{U}}\text{U}^{235}$  on fission gives energy

$$= 6.023 \times 32 \times 10^{12} \text{ J}$$

235 gm of  ${}_{92}^{\text{U}}\text{U}^{235}$  on fission gives energy

$$= \frac{6.023}{235} \times 3.2 \times 10^{12} \text{ J} = 8.20 \times 10^7 \text{ kJ}$$



$$b + d + 4x + 0y$$

$$\text{or } b = d + 4x$$

$$\text{or } x = \frac{(b - d)}{4}$$

$$a = c + 2x - y$$

$$\text{or } a = c + 2 \cdot \frac{(b - d)}{4} - y$$

$$\text{or } a = C + \frac{b - d}{2} - y$$

$$\text{or } y = (c - a) + \frac{(b - d)}{2}$$

93.  $t = \frac{2.303 t^{\frac{1}{2}}}{0.693} \log 1 + \frac{P^{206}}{U^{238}}$

$$t^{\frac{1}{2}} = 4.5 \times 10^9 \text{ year}$$

$$\text{moles of Pb} = \frac{20.6}{206} = 0.1$$

$$\text{moles of U}^{238} = \frac{23.8}{238} = 0.1$$

$$t = \frac{2.303 \times 4.5 \times 10^9 \text{ yr}}{0.693} \log \left( 1 + \frac{0.1}{0.1} \right)$$

$$= \frac{2.303 \times 4.5 \times 10^9 \text{ yr}}{0.693}$$

$$= \frac{2.303 \times 4.5 \times 10^9 \times 0.3010}{0.693}$$

$$= 4.5 \times 10^9 \text{ years.}$$

94.  $\lambda = \frac{0.693}{t^{\frac{1}{2}}} = \frac{0.693}{28.1} \text{ year}^{-1}$

$$N_0 = 1.0 \mu\text{g} = 10^{-6} \text{ g}$$

$$t = 20 \text{ year}$$

$$N = ?$$

$$\text{Apply } t = \frac{2.303}{\lambda} \log \frac{N_0}{N}$$

$$\log \frac{N_0}{N} = \frac{t \lambda}{2.303} = \frac{20 \times 0.693}{2.303 \times 28.1}$$

$$\log \frac{N_0}{N} = 0.2142$$

$$\frac{N_0}{N} = \text{antilog } 0.2142 = 1.637$$

$$\frac{N}{N_0} = \frac{1}{1.637} = 0.6108$$

$$N = N_0 \times 0.6108$$

$$= 10^{-6} \times 0.6108$$

$$= 0.6108 \mu\text{g}$$



## 11.40 ■ Nuclear Chemistry



(R)

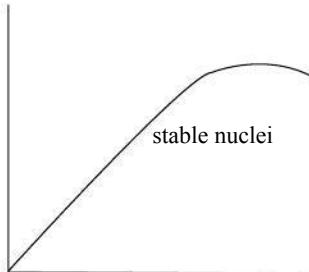
Hence P is isobar of Pb, Q and R are isobars and R is an isotope of Pb

### Assertion-Reason Type Questions

138. As  $T_{1/2}$  does not depend upon initial amount of substance so it remains 120 minutes
144. As charged particles can be accelerated by machines like cyclotron etc.
150. **Statement-1** The plot of atomic number (y-axis) versus number of neutrons (x-axis) for stable nuclei shows a curvature towards x-axis from the line of  $45^\circ$  slope as the atomic number is increased.

**Statement-2** Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons in heavier nuclides

[IIT 2008]

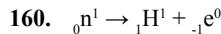


No. of neutrons

If the curve does not bend down towards the x-axis then the proton-proton repulsion would overcome the attractive forces of proton repulsion would overcome the attractive forces of proton and neutron. Hence, curve bends down to achieve stability

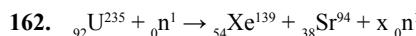
of the nuclei. In heavier nuclides, attractive forces between proton and neutron overcome proton-proton electrostatic repulsion.

### The IIT-JEE Corner



so it is equivalent to increase of one proton and decrease of one neutron

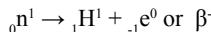
160. In positron emission and K-electron capture, proton is consumed so atomic number decrease



$$235 + 1 = 139 + 94 + x$$

$$x = 236 - 233 = 3.$$

164. n/p ratio of  $\text{Na}^{24}$  nuclide is 13/11 i.e., greater than unity and hence it is radioactive. To achieve stability (by decreasing its n/p ratio), neutron is broken into proton and electron.



165. On positron emission from nucleus, proton converts into neutron therefore atomic number decreases by one but atomic mass remains constant.

$$\frac{\text{Atomic mass}}{\text{Atomic number}} = \frac{23}{10}$$



(6 $\alpha$ , 2 $\beta$ ), total 8 particles.

### Numericals for Practice

1. A star converts all its He in Oxygen. Find the amount of energy released per nucleus of oxygen.  $\text{He} = 4.0026 \text{ amu}$   $\text{O} = 15.9994 \text{ amu}$
- a. 7 MeV
  - b. 7.26 MeV
  - c. 5.12 MeV
  - d. 10.24 MeV
2. The half life period of radium is 1580 years. It remains 1/16 after
- a. 1580 years
  - b. 3160 years
  - c. 4740 years
  - d. 6320 years
3. Starting with a sample of pure  $^{66}\text{Cu}$ , 7/8 of it decays into Zn in 15 minutes the corresponding half life is
- a. 7 1/2 min
  - b. 15 min
  - c. 10 min
  - d. 5 min
4. What percentage of a radioactive substance remains after 6.00 half lives have elapsed?
- a. 5.06 %
  - b. 3.46 %
  - c. 1.56 %
  - d. 6.25 %

5. In one type of mutual annihilation of an electron and a positron, three  $\gamma$ -ray photons are produced. If each photon has an energy of 0.3404 MeV, what is the mass of the positron in a.m.u? (1 amu = 931.5 MeV)
- $10.96 \times 10^{-4}$
  - $5.48 \times 10^{-4}$
  - $1.096 \times 10^{-4}$
  - $54.8 \times 10^{-4}$
6. How long does it take for a sample of 21684Po to decay by 70% from its original mass? Its half-life is 0.16 s.
- 0.28 s
  - 0.43 s
  - 0.082 s
  - 0.12 s
7. The radius of  $^{27}_{13}\text{Al}$  is 3.6 Fermi. Find the radius of  $^{125}_{52}\text{Te}$  nucleus.
- 8 Fermi
  - 4 Fermi
  - 5 Fermi
  - 6 Fermi
8. Radium-226, which undergoes alpha decay, has a half-life of 1622 yr. How many alpha particles are emitted in 1.0 min by a 5.0 mg sample of  $^{226}\text{Ra}$ ?
- $1.1 \times 10^9$
  - $1.1 \times 10^{10}$
  - $2.2 \times 10^9$
  - $5.5 \times 10^{10}$
9. The half life of a radio-isotope is three hours. If the mass of the undecayed isotope at the end of 18 hours is 4.125 gm, what was its mass initially?
- 132 g
  - 264 g
  - 180 g
  - 462 g
10. Find the binding energy of  $^{62}_{28}\text{Ni}$ . Given  $m_{\text{H}} = 1.008 \text{ u}$ ,  $m_n = 1.0087 \text{ u}$ ,  $m_{^{62}\text{Ni}} = 61.9238 \text{ u}$
- 695.3 MeV
  - 645.3 MeV
  - 595.3 MeV
  - 545.3 MeV
11. The half life of a radioactive isotope is three hours. If the initial mass of the isotope were 256 g, the mass of it remaining undecayed after 18 hours would be
- 4.0 g
  - 8.0 g
  - 12.0 g
  - 16.0 g
12. At radioactive equilibrium, the ratio between the atoms of two radioactive elements (X) and (Y) was found to be  $3.2 \times 10^9 : 1$  respectively. If half life of the element (X) is  $1.92 \times 10^{10}$  years, then half life of the element (Y) would be
- $6 \times 10^9$  years
  - $3.2 \times 10^9$  years
  - 6 years
  - $1.92 \times 10^{10}$  years
13. The half-life of the nucleus  $^{222}_{86}\text{Rn}$  is 3.88 days. How many mg of a 5000 mg sample of  $^{222}_{86}\text{Rn}$  remain after sixty days?
- 2168 mg
  - 4000 mg
  - 0.110 mg
  - 1.213 mg
14. When  $^{7}_{3}\text{Li}$  ( $M_{\text{Li}} = 7.016004 \text{ u}$ ) is bombarded by a proton two  $\alpha$ -particles result ( $M_{\text{He}} = 4.00260 \text{ u}$ ). Find the reaction energy.
- 17.35 MeV
  - 16.08 MeV
  - 13.35 MeV
  - 14.85 MeV
15. What mass of  $^{235}_{92}\text{U}$  has to undergo fission each day to provide 3000MeV power each day?
- 32 kg
  - 3.2 kg
  - 3.2 g
  - 320 g
16. Energy equivalent of 0.001 mg is
- $9 \times 10^7$  ergs
  - $9 \times 10^9$  ergs
  - $9 \times 10^7$  J
  - $9 \times 10^5$  J
17. A bone fragment found in a cave contains 0.21 times as much  $^{14}_{6}\text{C}$  as an equal amount of carbon in air when the organism containing bone died. Find the approximate age of fragment  $t_{1/2}$  of  $^{14}\text{C} = 5730$  years.
- $1.3 \times 10^4$  y
  - $1.15 \times 10^4$  y
  - $1.4 \times 10^4$  y
  - $1.24 \times 10^4$  y
18. The half-life of a radioactive nuclide is 0.693 minutes. The time (in minutes) required for the disintegration of this nuclide from 10 grams to one gram is .....
- 1
  - 0.693
  - 6.93
  - 2.303
19. The half life of  $^{226}\text{Ra}$  is 1602 year. Calculate the activity of 0.1 g of  $\text{RaCl}_2$  assuming all the Ra atoms are  $^{226}\text{Ra}$  and mass of Cl atom is 35.5 g/mol.
- $2.8 \times 10^9$  dps
  - $1.8 \times 10^9$  dps
  - $2.8 \times 10^8$  dps
  - $1.8 \times 10^8$  dps
20. The half-life of isotopic C-14 is 5760 years. Its mean life is
- 8254 years
  - 8524 years
  - 8640 years
  - 8420 years
21. A vessel of 125 cc contains  $^{3}_{1}\text{H}$  ( $t_{1/2} = 12.3$  y) at 500 kPa and 300 K. Find the activity of the gas.
- 724 Ci
  - 72.4 Ci
  - 0.754 Ci
  - 7.24 Ci

## 11.42 ■ Nuclear Chemistry

22. Neptunium-239 has a half life of 2.35 days. How many days must elapse for a sample of  $^{239}\text{Np}$  to decay to 1.00% of its original quantity?
- a. 10.6 days      b. 15.6 days  
c. 0.16 days      d. 25.6 days
23. Calculate the energy which can be obtained from 1 kg of  $\text{H}_2\text{O}$  through the fusion reaction  $^2_1\text{H} + ^2_1\text{H} \rightarrow ^3_1\text{H} + \text{P}$ . Assume  $1.5 \times 10^{-2}$  % of the water contains deuterium. The whole deuterium is consumed in the fusion reaction.
- a.  $2820 \times 10^4 \text{ J}$       b.  $2820 \text{ J}$   
c.  $2820 \times 10^8 \text{ J}$       d.  $2820 \times 10^6 \text{ J}$
24. The half-life for the process  $^{238}\text{U} \rightarrow ^{206}\text{Pb}$  is  $4.5 \times 10^9$  yr. A mineral sample contains 50.0 mg of  $^{238}\text{U}$  and 14.0 mg of  $^{206}\text{Pb}$ . What is the age of the mineral?
- a.  $1.8 \times 10^9 \text{ years}$   
b.  $1.8 \times 10^{10} \text{ years}$   
c.  $3.6 \times 10^9 \text{ years}$   
d.  $3.6 \times 10^9 \text{ years}$
25. A human body excretes certain material by a law similar to radioactivity. The body excretes half the amount injected in 24 h. Find the time in which activity falls to  $3 \mu\text{Ci}$ . If a person is injected technetium ( $t_{1/2} = 6\text{h}$ ) and its activity just after the injection is  $6 \mu\text{Ci}$ .
- a. 6 h      b. 6.3 h  
c. 4.8 h      d. none of these

### ANSWER KEYS

Q.	Ans.								
1.	d	2.	d	3.	d	4.	c	5.	b
6.	a	7.	d	8.	b	9.	b	10.	d
11.	a	12.	c	13.	c	14.	a	15.	b
16.	c	17.	a	18.	d	19.	a	20.	a
21.	a	22.	b	23.	d	24.	a	25.	c

### Hints and Explanations

1.  $E = \Delta mc^2$   
 $= [4 \times 4.0026 - 15.9994] 931.5$   
 $= 10.24 \text{ MeV}$

2.  $N = N_0 \times (\frac{1}{2})^n$   
 $1/16 = 1 \times (\frac{1}{2})^n$   
 $n = 4$

$t = n \times t_{1/2}$   
 $= 4 \times 1580 = 6320 \text{ years}$

3. Sample left =  $1/8 = 3$   
 $\text{So } n = 3 \text{ i.e., 3 half lines have passed}$   
 $3t_{1/2} = 15 \text{ or } t_{1/2} = 5 \text{ min.}$

5. Energy of three  $\gamma$ -ray photons  
 $= 3 \times 0.3404 \text{ MeV} = 1.0212 \text{ MeV}$   
 $= \frac{1.0212}{931.5} \text{ a.m.u.}$

which is the total mass of one electron and one positron.  
Therefore the mass of one positron

$$= \frac{1.0212}{931.5 \times 2} = 5.48 \times 10^{-4} \text{ a.m.u}$$

$$7. \quad \frac{R_1}{R_2} = \frac{A_1^{1/3}}{A_2^{1/3}}$$

$$R_2 = \left( \frac{125}{27} \right)^{1/3} \times 3.6 = 6 \text{ Fermi}$$

$$9. \quad 18 \text{ hrs} = 6 \text{ half-lives}$$

$$(1/2)^6 = \frac{4.125}{m_0 \text{ g}} \text{ g}$$

Here  $m_0 \text{ g}$  is the initial mass.

$$\frac{1}{64} = \frac{4.125}{m_0}$$

$$m_0 = 264 \text{ g}$$

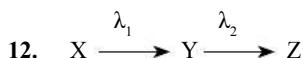
$$10. \quad E_B = (28 m_H + 34 m_n - 61.9238) 931.5 \\ = 545.3 \text{ MeV}$$

$$11. \quad C = C_0 (\frac{1}{2})^y$$

$$y = \frac{\text{total time}}{T_{1/2}} = \frac{18}{3} = 6$$

$$C_0 = 256$$

$$C(\text{undecayed}) = 256 (\frac{1}{2})^6 = \frac{256}{64} = 4 \text{ g}$$



At radioactive equilibrium,

$$(\lambda_X) \times (N_X) = (\lambda_Y) \times (N_Y)$$

$$\lambda_X / \lambda_Y = N_Y / N_X$$

$$\frac{(t_{1/2})_Y}{(t_{1/2})_X} = \frac{N_Y}{N_X} \text{ or } \frac{(t_{1/2})_Y}{1.92 \times 10^{10}} = \frac{1}{3.2 \times 10^9}$$

$$(t_{1/2})_Y = 6 \text{ years}$$

$$14. \quad Q = [7.016004 + 1.007825 - 2(4.002603)] \times 931.5 \\ = 0.81623 \times 931.5 \\ = 17.35 \text{ MeV}$$

15. 1 fission of 235- U gives 200MeV .

$$\text{Mass of uranium} = \frac{m \times 200 \times 1.6 \times 10^{13}}{235 \times 1.66 \times 10^{27}} \\ = 10^6 \times 3000 \times 86400 \text{ or} \\ m = 3.2 \text{ kg}$$

$$16. \quad E = mc^2$$

$$= 0.001 \text{ mg} \times \frac{10^{-3}}{1 \text{ mg}} \text{ g} \times \frac{1 \text{ kg}}{10^3 \text{ g}} \times (3.0 \times 10^8 \text{ m/s})^2 \\ = 1 \times 10^{-9} \times 9 \times 10^{16} \text{ kg m}^2 \text{ s}^{-2} \\ = 9 \times 10^7 \text{ J.}$$

$$17. \quad \lambda = \frac{0.693}{t_{1/2}}$$

$$= \frac{0.693}{5730}$$

$$= 1.209 \times 10^4 \text{ y}^{-1}$$

$$\frac{N}{N_0} = e^{-\lambda t} = 0.21 \text{ or } t = \frac{2.303 \log 1}{0.21/\lambda}$$

$$t = \frac{2.303 (0.6794)}{1.209 \times 10^{-4}}$$

$$= \frac{1.564 \times 10^4}{1.2}$$

$$= 1.3 \times 10^4 \text{ y}$$

$$18. \quad T = \frac{2.303 \times t_{1/2}}{0.693} \log_{10} N_0$$

$$= \frac{2.303 \times 0.693}{0.693} \log \frac{10}{1}$$

$$= 2.303 \text{ minutes}$$

19. Number of 226Ra atoms present

$$= \frac{0.1}{297} \times 6.02 \times 10^{23}$$

$$\text{Activity} = \lambda N$$

$$= \frac{0.693}{0.602 \times 3.156 \times 10^7} \times \frac{1}{297} 6.02 \times 10^{22}$$

$$= 2.8 \times 10^9 \text{ dps}$$

$$20. \quad \frac{0.693}{\lambda} = 5760 \text{ years}$$

$$\text{So mean life } \frac{1}{\lambda} = \frac{5760}{0.693} = 8311.6 \text{ years.}$$

$$21. \quad PV = nRT \text{ or number of moles } n = \frac{PV}{RT}$$

$$n = \frac{500 \times 10^3 \times 125 \times 10^{-6}}{8.31 \times 300}$$

$$= 25 \times 10^{-3}$$

**11.44 ■ Nuclear Chemistry**

$$\text{Activity } A = \lambda N$$

$$= \frac{0.693 \times 25 \times 10^{-3} \times 6.02 \times 10^{23}}{12.3 \times 3.156 \times 10^7 \times 3.7 \times 10^{10}}$$

$$= 724$$

23.  $D_2O = 1 \times 1.5 \times 10^{-4} \text{ kg} = 0.15 \text{ g}$

$$\text{Number of } {}^2{}_1H = \frac{0.15 \times 6.023 \times 10^{23}}{20}$$

$$= 4.5 \times 10^{21}$$

$$Q = (2 \times 2.014102 - 3.016049 - 1.008) 931.5 \times 4.5 \times 10^{21} \times 1.6 \times 10^{-13} \text{ J}$$

$$= 0.004055 \times 931.5 \times 7.2 \times 10^8 = 2820 \text{ MJ}$$

25.  $\frac{1}{t} = \frac{1}{t_1} + \frac{1}{t_2}$

$$t = \frac{t_1 t_2}{t_1 + t_2} = \frac{24 \times 6}{24 + 6}$$

$$= 4.8 \text{ h}$$