

**BRILLIANT PUBLIC SCHOOL,
SITAMARHI**
(Affiliated up to +2 level to C.B.S.E., New Delhi)



Class-XII

IIT-JEE Advanced Chemistry

Study Package

Session: 2014-15

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STUDY PACKAGE

Target: IIT-JEE (Advanced)

SUBJECT: CHEMISTRY-XII

Chapters:

- 1. Solid State**
- 2. Solutions**
- 3. Surface Chemistry**
- 4. Chemical Kinetics**
- 5. Thermochemistry**
- 6. Electrochemistry**

STUDY PACKAGE

Target: IIT-JEE (Advanced)

SUBJECT: CHEMISTRY-XII

TOPIC: 13. Solid State

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- 2. Exercise I**
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- 7. 34 Yrs. Que. from IIT-JEE**
- 8. 10 Yrs. Que. from AIEEE**

THE KEY

Crystalline solids:

Crystalline solids are those whose atom, molecules or ions have an ordered arrangement extending over a **Long Range**. example-(Rock salt, NaCl).

Amorphous solids:

Amorphous solids are those whose constituent particles are randomly arranged and have no ordered long range structure. example: Rubber, Glass etc.

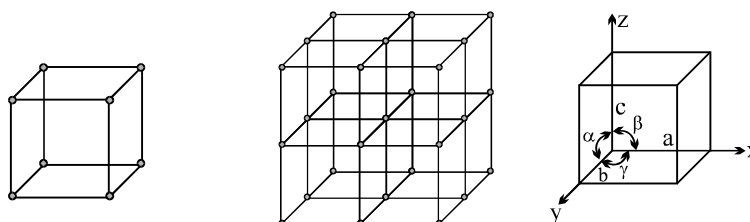
TYPES OF CRYSTALLINE SOLIDS:

Type of Solid	Intermolecular forces	Properties	Examples
Ionic	Ion-Ion forces	Brittle, hard high Melting	NaCl, KCl, MgCl_2
Molecular	Dispersion forces/Dipole-Dipole /H-bond	Soft, low melting non-conducting	H_2O , Br_2 , CO_2 , CH_4
Covalent network	Covalent bonds	Hard: High melting	C-Diamond SiO_2
Metallic	Metallic bonds	Variable hardness and melting point conducting	Na, Zn, Cu, Fe

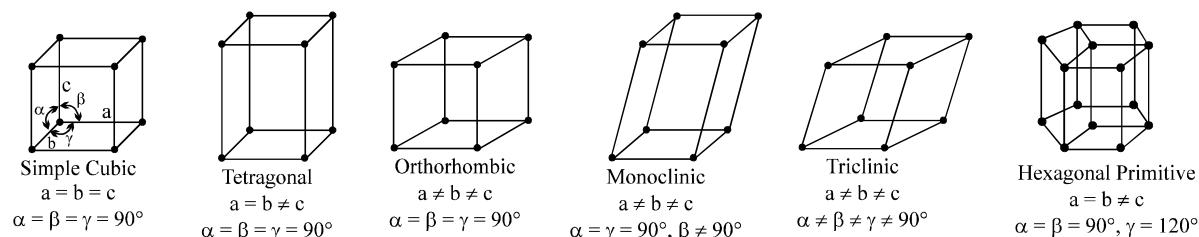
TYPES OF UNIT CELL:

Collection of lattice points, whose repetition produce whole lattice is called a unit cell. The whole lattice can be considered to be made by repetition of unit cell.

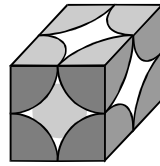
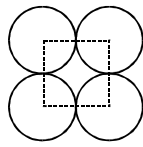
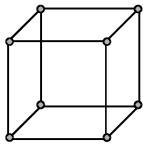
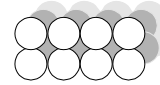
1. Unit Cell:



Crystal Systems		Bravais Lattice	Unit Cell Parameters	
			Intercepts	Crystal Angles
1	Cubic	Primitive, Face Centered, Body Centered	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
2	Orthorhombic	Primitive, Face Centered, Body Centered, End Centered	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
3	Rhombohedral	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
4	Monoclinic	Primitive, End Centered	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$
5	Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$
6	Tetragonal	Primitive, Body Centered	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
7	Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$

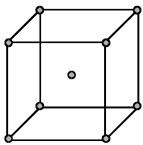


- 1.1 Primitive or simple cubic (PS/SC) unit cell:** Spheres in one layer sitting directly on top of those in previous layer, so that all layers are identical. Each sphere is touched by six other, hence coordination number is 6. 52% of available space occupied by spheres.
Example: Polonium crystallises in simple cubic arrangement.



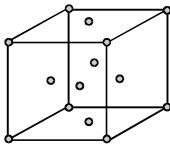
$$Z = 1 ; \text{C.N.} = 6$$

- 1.2 Body Centered cubic (BCC) unit cell:** Spheres in one layer sit in the depression made by first layer in a-b-a-b manner. Coordination number is 8, and 68% of available space is occupied by atoms.
Example: Iron, sodium and 14 other metal crystallises in this manner.



$$Z = 2 ; \text{C.N.} = 8$$

- 1.3 Face centered cubic (FCC) unit cell:**
Examples : Al, Ni, Fe, Pd all solid noble gases etc.

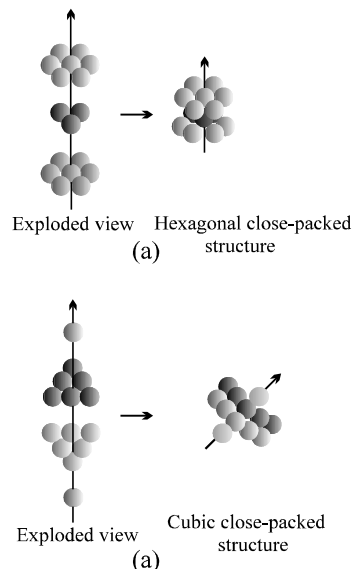
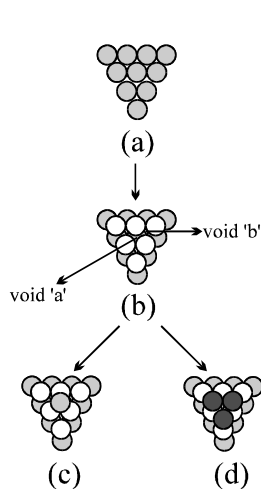


$$Z = 4 ; \text{C.N.} = 12$$

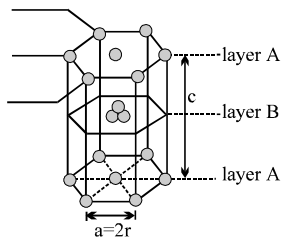
2. Density of cubic crystals:

TYPE OF PACKING:

- 3. Closest packing of atoms:** This is the most efficient way of packing 74% of available space is occupied by spheres and coordination number is 12.
- Hexagonal close pack (A-B-A-B) type packing :** Each layer has hexagonal arrangement of touching sphere and 3rd layer is similar (exactly on top) of first layer.
 - Cubic close pack (A-B-C-A-B-C):** AB layers are similar to HCP arrangement but third layer is offset from both A and B layers. The fourth layer is exactly on top of first layer.

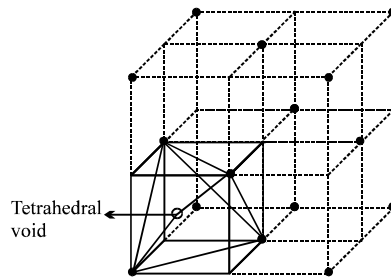
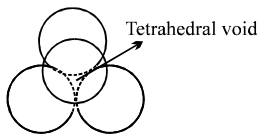


Hexagonal primitive unit cell



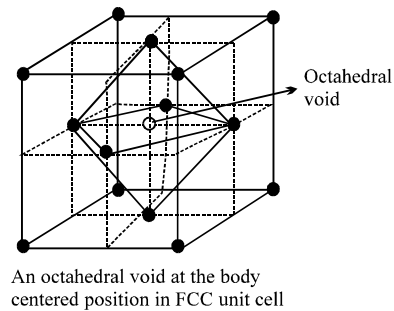
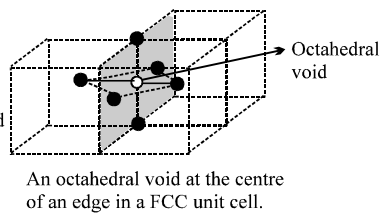
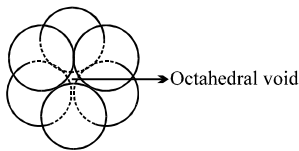
4. Types of voids

4.1 Tetrahedral void

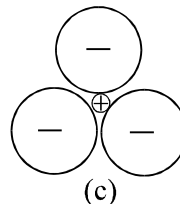
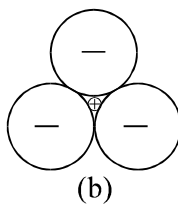
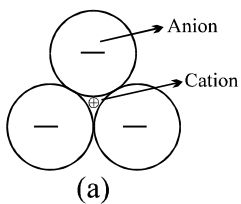


Number of tetrahedral voids per FCC unit cell

4.2 Octahedral void

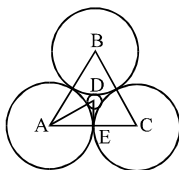


5. Radius ratio



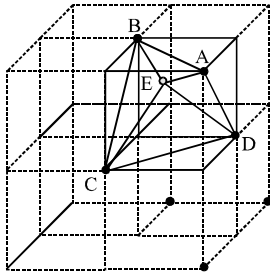
5.1 Radius ratio for co-ordination number 3

(Triangular Arrangement): $r^+ + r^- = \frac{2}{3} \sqrt{3} r^-$; $\frac{r^+}{r^-} = \frac{2-\sqrt{3}}{\sqrt{3}} = 0.155$



5.2 Radius ratio for coordination number 4

(Tetrahedral arrangement): $r^+ + r^- = \frac{\sqrt{3}a}{4}$; $4r^- = \sqrt{2} a = \frac{\sqrt{3}}{\sqrt{2}} r^+$



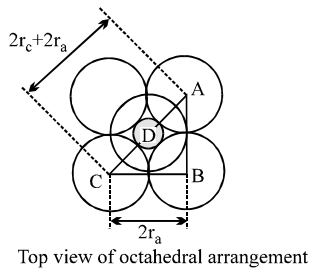
$$\frac{r^+}{r^-} = \frac{\sqrt{3}-\sqrt{2}}{\sqrt{2}} = 0.225$$

5.3 Radius ratio for coordination number 6: $r^+ + r^- = \sqrt{2} r^-$

(Octahedral Arrangement) or

$$\frac{r^+}{r^-} = \sqrt{2} - 1 = 0.414$$

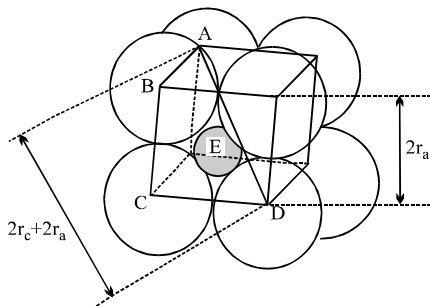
Radius ratio for coordination number 4
(Square planar arrangement)



5.4 Radius ratio for coordination number 8: $r^+ + r^- = \frac{\sqrt{3}}{2} a$

(Body centered cubic crystal)

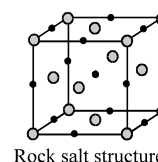
$$r^+ + r^- = \sqrt{3} r^-$$



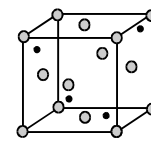
$$\frac{r^+}{r^-} = \sqrt{3} - 1 = 0.732$$

6. Types of ionic structures

6.1 **Rock salt structure:** (NaCl) Larger atom form ccc arrangement and smaller atom filling all octahedral voids.

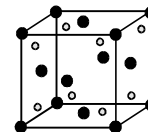


- 6.2 Zinc blende (sphalerite) structure:** (ZnS) Larger atom form cc arrangement and smaller atom filling half of alternate tetrahedral voids



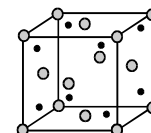
Zinc blende structure

- 6.3 Fluorite structure:** (CaF₂) Ca²⁺ forming ccp arrangement and F⁻ filling all tetrahedral voids.



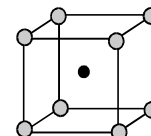
Fluorite structure

- 6.4 Antifluorite structure :** (Li₂O) O²⁻ ion forming ccp and Li⁺ taking all tetrahedral voids.



Antifluorite structure

- 6.5 Cesium halide structure:** (CsCl) Cl⁻ at the corners of cube and Cs⁺ in the center.

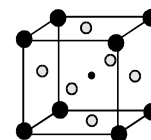


Cesium chloride structure

- 6.6 Corundum Structure:** (Al₂O₃) O²⁻ forming hcp and Al³⁺ filling 2/3 octahedral voids.

- 6.7 Rutile structure:** (TiO₂) O²⁻ forming hcp while Ti⁴⁺ ions occupy half of the octahedral voids.

- 6.8 Perovskite structure:** (CaTiO₃) Ca²⁺ in the corner of cube O²⁻ at the face center and Ti⁴⁺ at the centre of cube.



Perovskite structure

- 6.9 Spinel and inverse spinel structure:** (MgAl₂O₄) O²⁻ forming fcc, Mg²⁺ filling 1/8 of tetrahedral voids and Al³⁺ taking half of octahedral voids. In an inverse spinel structure, O²⁻ ion form FCC lattice, A²⁺ ions occupy 1/8 of the tetrahedral voids and trivalent cation occupies 1/8 of the tetrahedral voids and 1/4 of the octahedral voids.

7. Crystal defects:

Point defects: When ions or atoms do not hold the theoretical position, this is called point defect. Point defects are of two types:

(I) *Stoichiometric defects:*

- (a) **Schottky defect:** Due to missing of ions from lattice point in pairs.

- (b) **Frenkel defect:** It is caused due to the creation of lattice vacancy as a result of misplaced ion in interstitial site.

★ Schottky defect common in ionic solid with high coordination number. NaCl, KCl, KBr

★ Frenkel defect :- Solid with low coordination number ZnS, AgBr.

(II) *Non-Stoichiometric defects:* Ratio of positive and negative ion differ from that indicated by chemical formula.

★ **Metal-excess defect :**

- (a) A negative ion replaced by electron. (F-centre)

- (b) Extra metal ion present in lattice and electron also present in interstitial site.

★ **Metal-deficiency defect caused by :** Cation missing from lattice point, electroneutrality maintained by metal ions with higher oxidation state as Fe_{0.94}°O.

THE ATLAS

TYPES OF SOLIDS

Crystalline Solids

Crystalline solids have long range order i.e. the constituent particles are arranged in a regular fashion and this symmetrical arrangement extends throughout the crystal length.

Amorphous Solids

Lattice - Unit Cells

- (i) A unit cell is the smallest repeating structural unit the crystalline solid. Bravais has predicted that there are only 14 unit cells that exists in nature.
- (ii) The relation between the edge length (a) and the radius of atom (r) forming lattice are as follows. PC : $a=2r$, BCC: $\sqrt{3}a=4r$; FCC: $\sqrt{2}a=4r$ & HP: $a=2r$ height(c) = $4r\sqrt{\frac{2}{3}}$

Packing fraction and density determination

- (i) The ratio of volume occupied by the effective atoms to the volume of the unit cell is called packing fraction. Its values for various unit cells are PC = 0.52, BCC = 0.68, FCC & HP = 0.74.
- (ii) Density (ρ) of cubic crystal is calculated using the relation $\rho = \frac{n \times M}{N_{AV} \times a^3}$ where
 n =number of effective atoms, M =Atomic mass, N_{AV} =Avogadro's number and a = Edge length.

Type of void and radius ratio rule

- (i) Tetrahedral & octahedral voids are present only in closest packed structures. The effective number of octahedral voids in a unit cell is equal to the effective number of atoms in the unit cell & effective number of tetrahedral voids is equal to double the number of effective atoms in the unit cell.
- (ii) The sum of radius of the atom of host lattice (r_h) and the radius of atom occupying void ($r_{f(i)}$ or $r_{f(o)}$) is given by
For octahedral void, $r_h + r_{f(o)} = \frac{a}{2}$ & for tetrahedral void, $r_h + r_{f(i)} = \frac{\sqrt{3}a}{4}$
- (iii) Limiting radius is defined as the minimum ratio of cation to anion radius. It is defined when cation is in contact with anions and anions are also in contact with each other.
- (iv) Radius ratio depends on the co-ordination number. The limiting radius ratio for the various co-ordination numbers are
C.N.3 : 0.155, C.N.4 (Tetrahedral) : 0.225, C.N.4 (Square planar) : 0.414,
C.N.6 (Octahedral) : 0.414, C.N.8 (BCC) : 0.732, C.N.12 (Ideal FCC) : 1

Defects in Solids

Ionic lattice has 2 major defects. Schottky defect occurs due to the cation-anion pair vacancy, which decreases the density of crystal. Frenkel defect occurs when an ion leaves its lattice site and fits into an interstitial space. Due to Frenkel defect, density of crystal remains unaffected.

EXERCISE I

Formula of ionic solid from unit cell description

- Q.1 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. What is the formula of compound.
- Q.2 A compound alloy of gold and copper crystallizes in a cubic lattice in which gold occupy that lattice point at corners of the cube and copper atom occupy the centres of each of the cube faces. What is the formula of this compound.
- Q.3 A cubic solid is made by atoms A forming close pack arrangement, B occupying one-fourth of tetrahedral void and C occupying half of the octahedral voids. What is the formula of compound.
- Q.4 What is the percent by mass of titanium in rutile, a mineral that contains Titanium and oxygen, if structure can be described as a close packed array of oxide ions, with titanium in one half of the octahedral holes. What is the oxidation number of titanium?
- Q.5 Spinel is an important class of oxides consisting of two types of metal ions with the oxide ions arranged in CCP pattern. The normal spinel has one-eighth of the tetrahedral holes occupied by one type of metal ion and one half of the octahedral hole occupied by another type of metal ion. Such a spinel is formed by Zn^{2+} , Al^{3+} and O^{2-} , with Zn^{2+} in the tetrahedral holes. Give the formulae of spinel.

Edge length, density and number of atoms per unit cell

- Q.6 KF crystallizes in the NaCl type structure. If the radius of K^+ ions is 132 pm and that of F^- ion is 135 pm, what is the shortest K–F distance? What is the edge length of the unit cell? What is the closest K–K distance?
- Q.7 A closed packed structure of uniform spheres has the edge length of 534 pm. Calculate the radius of sphere, if it exists in
(a) simple cubic lattice (b) BCC lattice (c) FCC lattice
- Q.8 Calculate the density of diamond from the fact that it has face centered cubic structure with two atoms per lattice point and unit cell edge length of 3.569 Å.
- Q.9 An element crystallizes into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two atoms on one of its body diagonals. If the volume of this unit cell is $24 \times 10^{-24} \text{ cm}^3$ and density of element is 7.2 g cm^{-3} , calculate the number of atoms present in 200 g of element.
- Q.10 Silver has an atomic radius of 144 pm and the density of silver is 10.6 g cm^{-3} . To which type of cubic crystal, silver belongs?
- Q.11 AgCl has the same structure as that of NaCl. The edge length of unit cell of AgCl is found to be 555 pm and the density of AgCl is 5.561 g cm^{-3} . Find the percentage of sites that are unoccupied.

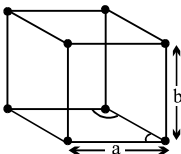
- Q.12 Xenon crystallises in the face-centred cubic lattice and the edge of the unit cell is 620 pm. What is the nearest neighbour distance and what is the radius of xenon atom?
- Q.13 The two ions A^+ and B^- have radii 88 and 200 pm respectively. In the closed packed crystal of compound AB, predict the co-ordination number of A^+ .
- Q.14 CsCl has the bcc arrangement and its unit cell edge length is 400 pm. Calculate the interionic distance in CsCl.
- Q.15 Gold crystallizes in a face centered cubic lattice. If the length of the edge of the unit cell is 407 pm, calculate the density of gold as well as its atomic radius assuming it to be spherical. Atomic mass of gold = 197 amu.
- Q.16 The density of KBr is 2.75 g cm^{-3} . The length of the edge of the unit cell is 654 pm. Show that KBr has face centered cubic structure.
($N = 6.023 \times 10^{23} \text{ mol}^{-1}$, At. mass : K = 39, Br = 80)
- Q.17 An element crystallizes in a structure having FCC unit cell of an edge 200 pm. Calculate the density, if 200 g of this element contains 24×10^{23} atoms.
- Q.18 The effective radius of the iron atom is 1.42 \AA . It has FCC structure. Calculate its density (Fe = 56 amu)
- Q.19 A crystal of lead(II) sulphide has NaCl structure. In this crystal the shortest distance between Pb^{+2} ion and S^{2-} ion is 297 pm. What is the length of the edge of the unit cell in lead sulphide? Also calculate the unit cell volume.
- Q.20 If the length of the body diagonal for CsCl which crystallises into a cubic structure with Cl^- ions at the corners and Cs^+ ions at the centre of the unit cells is 7 \AA and the radius of the Cs^+ ion is 1.69 \AA , what is the radii of Cl^- ion?

PROFICIENCY TEST

1. Crystalline solids are isotropic.
2. Rhombohedral, triclinic and hexagonal are the unit cells, which have only primitive arrangement possible.
3. Packing fraction of FCC and HP units cells are same.
4. The minimum void fraction for any unit cell in any shape having only one type of atom and all voids unfilled is 0.26.
5. Packing fraction of a lattice structure depends on the radius of the atom crystallizing in it.
6. The location of tetrahedral voids in FCC unit cell are the centers of 8 minicubes forming a large cube.
7. Effective number of octahedral voids in a unit cell is equal to the effective number of atoms in the unit cell.
8. Radius ratio for co-ordination number 4 having tetrahedral and square planar geometry is same.
9. The radius ratio value for co-ordination number 4 having square planar geometry and co-ordination number 6 having octahedral geometry is same.
10. A metallic element crystallises into a lattice containing a sequence of layers of AB AB AB Any packing of spheres leaves out voids in the lattice 26% percent by volume of this lattice is empty space.
11. The relation between edge length (a) and radius of atom (r) for BCC lattice is_____.
12. The relation between edge length (a) and radius of atom (r) for FCC lattice is_____.
13. ABCABC.....layering pattern is called _____ packing, found in _____ lattice.
14. ABABAB.....layering pattern is called _____ packing , found in _____ lattice.
15. Height (c) of the hexagonal primitive unit cell in terms of radius of atom (r) is_____.
16. Anions would be in contact with each other only if the cation to anion radius for a given co-ordination number is_____.
17. The number of tetrahedral voids in hexagonal primitive unit cell is_____.
18. The limiting radius for co-ordination number 8 is_____.
19. For cesium chloride structure, the interionic distance (in terms of edge length, a) is equal to _____.
20. Density of a crystal ____due to Schottky defect and ____due to Frankel defect.

EXERCISE II

- Q.1 Iron has body centered cubic lattice structure. The edge length of the unit cell is found to be 286 pm. What is the radius of an iron atom?
- Q.2 Cesium chloride forms a body centered cubic lattice. Cesium and chloride ions are in contact along the body diagonal of the unit cell. The length of the side of the unit cell is 412 pm and Cl^- ion has a radius of 181 pm. Calculate the radius of Cs^+ ion.
- Q.3 In a cubic closed packed structure of mixed oxides the lattice is made up of oxide ions, one eighth of tetrahedral voids are occupied by divalent ions (A^{2+}) while one half of the octahedral voids occupied trivalent ions (B^{3+}). What is the formula of the oxide?
- Q.4 A solid A^+ and B^- had NaCl type closed packed structure. If the anion has a radius of 250 pm, what should be the ideal radius of the cation? Can a cation C^+ having a radius of 180 pm be slipped into the tetrahedral site of the crystal of A^+B^- ? Give reasons for your answer.
- Q.5 Calculate the value of Avogadro's number from the following data:
Density of NaCl = 2.165 cm^{-3}
Distance between Na^+ and Cl^- in NaCl = 281 pm.
- Q.6 If the radius of Mg^{2+} ion, Cs^+ ion, O^{2-} ion, S^{2-} ion and Cl^- ion are 0.65 \AA , 1.69 \AA , 1.40 \AA , 1.84 \AA , and 1.81 \AA respectively. Calculate the co-ordination numbers of the cations in the crystals of MgS, MgO and CsCl.
- Q.7 Iron occurs as bcc as well as fcc unit cell. If the effective radius of an atom of iron is 124 pm. Compute the density of iron in both these structures.
- Q.8 KCl crystallizes in the same type of lattice as does NaCl. Given that $\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = 0.5$ and $\frac{r_{\text{Na}^+}}{r_{\text{K}^+}} = 0.7$ Calculate:
(a) The ratio of the sides of unit cell for KCl to that for NaCl and
(b) The ratio of densities of NaCl to that for KCl.
- Q.9 An element A (Atomic weight = 100) having bcc structure has unit cell edge length 400 pm. Calculate the density of A and number of unit cells and number of atoms in 10 gm of A.
- Q.10 Prove that the void space percentage in zinc blende structure is 25%.
- Q.11 A unit cell of sodium chloride has four formula units. The edge of length of the unit cell is 0.564 nm. What is the density of sodium chloride.
- Q.12 In a cubic crystal of CsCl (density = 3.97 gm/cm^3) the eight corners are occupied by Cl^- ions with Cs^+ ions at the centre. Calculate the distance between the neighbouring Cs^+ and Cl^- ions.
- Q.13 KF has NaCl structure. What is the distance between K^+ and F^- in KF if density of KF is 2.48 gm/cm^3 .
- Q.14 The composition of a sample of wustite is $\text{Fe}_{0.93}\text{O}_{1.0}$. What percentage of iron is present in the form of Fe(III)?

- Q.15 BaTiO_3 crystallizes in the perovskite structure. This structure may be described as a cubic lattice with barium ions occupying the corner of the unit cell, oxide ions occupying the face-centers and titanium ion occupying the center of the unit cell.
- If titanium is described as occupying holes in BaO lattice, what type of holes does it occupy?
 - What fraction of this type hole does it occupy?
- Q.16 RbI crystallizes in bcc structure in which each Rb^+ is surrounded by eight iodide ions each of radius 2.17 \AA . Find the length of one side of RbI unit cell.
- Q.17 If NaCl is doped with $10^{-3} \text{ mol \% SrCl}_2$, what is the numbers of cation vacancies?
- Q.18 Find the size of largest sphere that will fit in octahedral void in an ideal FCC crystal as a function of atomic radius 'r'. The insertion of this sphere into void does not distort the FCC lattice. Calculate the packing fraction of FCC lattice when all the octahedral voids are filled by this sphere.
- Q.19 A cubic unit cell contains manganese ions at the corners and fluoride ions at the center of each edge.
- What is the empirical formula of the compound?
 - What is the co-ordination number of the Mn ion?
 - Calculate the edge length of the unit cell, if the radius of Mn ion is 0.65 \AA and that of F^- ion is 1.36 \AA .
- Q.20 NaH crystallizes in the same structure as that of NaCl . The edge length of the cubic unit cell of NaH is 4.88 \AA .
- Calculate the ionic radius of H^- , provided the ionic radius of Na^+ is 0.95 \AA .
 - Calculate the density of NaH .
- Q.21 Metallic gold crystallises in fcc lattice. The length of the cubic unit cell is $a = 4.07 \text{ \AA}$.
- What is the closest distance between gold atoms.
 - How many "nearest neighbours" does each gold atom have at the distance calculated in (a).
 - What is the density of gold?
 - Prove that the packing fraction of gold is 0.74.
- Q.22 Ice crystallizes in a hexagonal lattice. At the low temperature at which the structure was determined, the lattice constants were $a = 4.53 \text{ \AA}$, and $b = 7.60 \text{ \AA}$ (see figure). How many molecules are contained in a given unit cell? [density (ice) = 0.92 gm/cm^3)]
- Q.23 Using the data given below, find the type of cubic lattice to which the crystal belongs.
- | | Fe | V | Pd |
|-------------------------------|------|------|-------|
| a in pm | 286 | 301 | 388 |
| ρ in gm cm^{-3} | 7.86 | 5.96 | 12.16 |
- 
- Q.24 Potassium crystallizes in a body-centered cubic lattice with edge length, $a = 5.2 \text{ \AA}$.
- What is the distance between nearest neighbours?
 - What is the distance between next-nearest neighbours?
 - How many nearest neighbours does each K atom have?
 - How many next-nearest neighbours does each K atom have?
 - What is the calculated density of crystalline potassium?
- Q.25 Prove that void space in fluorite structure per unit volume of unit cell is 0.243.
- Q.26 A compound formed by elements X & Y, Crystallizes in a cubic structure, where X is at the corners of the cube and Y is at six face centers. What is the formula of the compound? If side length is 5 \AA , estimate the density of the solid assuming atomic weight of X and Y as 60 and 90 respectively.

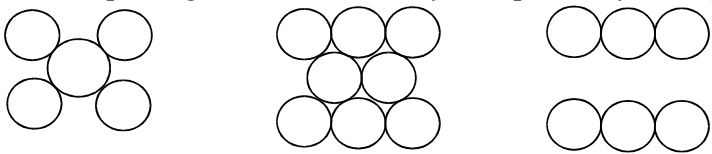
- Q.27 The metal nickel crystallizes in a face centred cubic structure. Its density is 8.9 gm/cm^3 . Calculate
- the length of the edge of the unit cell.
 - the radius of the nickel atom. [Atomic weight of Ni = 58.89]
- Q.28 The olivine series of minerals consists of crystals in which Fe and Mg ions may substitute for each other causing substitutional impurity defect without changing the volume of the unit cell. In olivine series of minerals, oxide ion exist as FCC with Si^{4+} occupying $\frac{1}{4}$ th of octahedral voids and divalent ions occupying $\frac{1}{4}$ th of tetrahedral voids. The density of forsterite (magnesium silicate) is 3.21 g/cc and that of fayalite (ferrous silicate) is 4.34 g/cc . Find the formula of forsterite and fayalite minerals and the percentage of fayalite in an olivine with a density of 3.88 g/cc .
- Q.29 The mineral hawleyite, one form of CdS , crystallizes in one of the cubic lattices, with edge length 5.87 \AA . The density of hawleyite is 4.63 g cm^{-3} .
- In which cubic lattice does hawleyite crystallize?
 - Find the Schottky defect in g cm^{-3} .
- Q.30 A strong current of trivalent gaseous boron passed through a germanium crystal decreases the density of the crystal due to part replacement of germanium by boron and due to interstitial vacancies created by missing Ge atoms. In one such experiment, one gram of germanium is taken and the boron atoms are found to be 150 ppm by weight, when the density of the Ge crystal decreases by 4%. Calculate the percentage of missing vacancies due to germanium, which are filled up by boron atoms.
Atomic wt. Ge = 72.6, B = 11

EXERCISE III

- Q.1 A solid has a structure in which W atoms are located at the corners of a cubic lattice, O atom at the centre of the edges and Na atom at centre of the cubic. The formula for the compound is
(A) NaWO_2 (B) NaWO_3 (C) Na_2WO_3 (D) NaWO_4
- Q.2 The density of CaF_2 (fluorite structure) is 3.18 g/cm^3 . The length of the side of the unit cell is
(A) 253 pm (B) 344 pm (C) 546 pm (D) 273 pm
- Q.3 Which of the following statements is correct in the rock-salt structure of an ionic compounds?
(A) coordination number of cation is four whereas that of anion is six.
(B) coordination number of cation is six whereas that of anion is four.
(C) coordination number of each cation and anion is four.
(D) coordination number of each cation and anion is six.
- Q.4 The coordination number of cation and anion in Fluorite CaF_2 and CsCl are respectively
(A) 8:4 and 6:3 (B) 6:3 and 4:4 (C) 8:4 and 8:8 (D) 4:2 and 2:4
- Q.5 The interstitial hole is called tetrahedral because
(A) It is formed by four spheres.
(B) Partly same and partly different.
(C) It is formed by four spheres the centres of which form a regular tetrahedron.
(D) None of the above three.
- Q.6 The tetrahedral voids formed by ccp arrangement of Cl^- ions in rock salt structure are
(A) Occupied by Na^+ ions (B) Occupied by Cl^- ions
(C) Occupied by either Na^+ or Cl^- ions (D) Vacant
- Q.7 The number of nearest neighbours around each particle in a face-centred cubic lattice is
(A) 4 (B) 6 (C) 8 (D) 12
- Q.8 If the anions (A) form hexagonal closest packing and cations (C) occupy only $2/3$ octahedral voids in it, then the general formula of the compound is
(A) CA (B) CA_2 (C) C_2A_3 (D) C_3A_2
- Q.9 A solid is formed and it has three types of atoms X, Y, 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) $\text{X}_2\text{Y}_4\text{Z}$ (B) XY_2Z_4 (C) $\text{X}_4\text{Y}_2\text{Z}$ (D) X_4YZ_2
- Q.10 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 cubic (B) Body centred cubic (C) Face centred cubic (D) None
- Q.11 A compound XY crystallizes in BCC lattice with unit cell edge length of 480 pm. If the radius of Y^- is 225 pm, then the radius of X^+ is
(A) 127.5 pm (B) 190.68 pm (C) 225 pm (D) 255 pm
- Q.12 The mass of a unit cell of CsCl corresponds to
(A) 1 Cs^+ and 1 Cl^- (B) 1 Cs^+ and 6 Cl^- (C) 4 Cs^+ and 4 Cl^- (D) 8 Cs^+ and 1 Cl^-

- Q.13 In the closest packing of atoms A (radius : r_a), the radius of atom B that can be fitted into tetrahedral voids is
 (A) $0.155 r_a$ (B) $0.225 r_a$ (C) $0.414 r_a$ (D) $0.732 r_a$
- Q.14 Which one of the following schemes of ordering closed packed sheets of equal sized spheres do not generate close packed lattice.
 (A) ABCABC (B) ABACABAC (C) ABBAABBA (D) ABCBCABCBC
- Q.15 An ionic compound AB has ZnS type structure. If the radius A^+ is 22.5 pm, then the ideal radius of B^- would be
 (A) 54.35 pm (B) 100 pm (C) 145.16 pm (D) none of these
- Q.16 NH_4Cl crystallizes in a body-centered cubic type lattice with a unit cell edge length of 387 pm. The distance between the oppositely charged ions in the lattice is
 (A) 335.1 pm (B) 83.77 pm (C) 274.46 pm (D) 137.23 pm
- Q.17 $r_{Na^+} = 95$ pm and $r_{Cl^-} = 181$ pm in NaCl (rock salt) structure. What is the shortest distance between Na^+ ions?
 (A) 778.3 pm (B) 276 pm (C) 195.7 pm (D) 390.3 pm
- Q.18 In diamond, carbon atom occupy FCC lattice points as well as alternate tetrahedral voids. If edge length of the unit cell is 356 pm, then radius of carbon atom is
 (A) 77.07 pm (B) 154.14 pm (C) 251.7 pm (D) 89 pm
- Q.19 Which of the following will show schottky defect
 (A) CaF_2 (B) ZnS (C) AgCl (D) CsCl
- Q.20 Give the correct order of initials **T** (true) or **F** (false) for following statements.
I. In an anti-fluorite structure anions form FCC lattice and cations occupy all tetrahedral voids.
II. If the radius of cations and anions are 0.2 \AA and 0.95 \AA then coordinate number of cation in the crystal is 4.
III. An atom/ion is transferred from a lattice site to an interstitial position in Frenkel defect.
IV. Density of crystal always increases due to substitutinal impurity defect.
 (A) TFFF (B) FTTF (C) TFFT (D) TFTF

EXERCISE IV

- Q.1 The edge length of unit cell of a metal having atomic 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. ($N_A = 6 \times 10^{23}$). Give the answer in pm. **[JEE 2006]**
- Q.2 An element crystallises in FCC lattice having edge length 400 pm. Calculate the maximum diameter which can be placed in interstitial sites without disturbing the structure. **[JEE 2005]**
- Q.3 Which of the following FCC structure contains cations in alternate tetrahedral voids?
 (A) NaCl (B) ZnS (C) Na₂O (D) CaF₂ **[JEE 2005]**
- Q.4(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⁻³.
 (ii) If measured density is 20 kg m⁻³. Identify the type of point defect. **[JEE-2004]**
- Q.5 Marbles of diameter 10 mm each are to be arranged on a flat surface so that their centres lie within the area enclosed by four lines of length each 40 mm. Sketch the arrangement that will give the maximum number of marbles per unit area, that can be enclosed in this manner and deduce the expression to calculate it. **[JEE-2003]**
- Q.6 A substance A_xB_y crystallises in a FCC lattice in which atoms “A” occupy each corner of the cube and atoms “B” occupy the centres of each face of the cube. Identify the correct composition of the substance A_xB_y.
 (A) AB₃ (B) A₄B₃
 (C) A₃B (D) composition cannot be specified **[JEE-2002]**
- Q.7 The figures given below show the location of atoms in three crystallographic planes in FCC lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram. **[JEE-2000]**
- 
- Q.8 In a solid “AB” having NaCl structure “A” atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axes are removed, then the resultant stoichiometry of the solid is
 (A) AB₂ (B) A₂B (C) A₄B₃ (D) A₃B₄ **[JEE-2000]**
- Q.9 In any ionic solid [MX] with schottky defects, the number of positive and negative ions are same. **[T/F]** **[JEE-2000]**
- Q.10 The coordination number of a metal crystallising in a hcp structure is **[JEE-2000]**
 (A) 12 (B) 4 (C) 8 (D) 6
- Q.11 A metal crystallises into two cubic phases, FCC and BCC whose unit cell lengths are 3.5 and 3.0 Å respectively. Calculate the ratio of densities of FCC and BCC. **[JEE-1999]**

- Q.12 Which of the following statements are correct :
(A) The coordination number of each type of ion in CsCl is 8.
(B) A metal that crystallises in BCC structure has a coordination number 12.
(C) A unit cell of an ionic crystal shares some of its ions with other unit cells
(D) The length of the unit cell in NaCl is 552 pm.
[$r_{\text{Na}^+} = 95 \text{ pm}$; $r_{\text{Cl}^-} = 181 \text{ pm}$] **[JEE-1998]**
- Q.13 In the sodium chloride structure, each Na^+ ion is surrounded by six Cl^- nearest neighbours and _____
 Na^+ ions next nearest neighbours. **[JEE-1997]**
- Q.14 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 sod. chloride. **[JEE-1997]**
- Q.15 Chromium crystallises with bcc lattice. The unit cell length is 287 pm. Calculate atomic rad. What would be the density of chromium. **[JEE-1997]**

ANSWER KEY

EXERCISE I

- Q.1 A-B Q.2 AuCu₃ Q.3 A₄B₂C₂ Q.4 59.95%, +4
Q.5 ZnAl₂O₄ Q.6 267 pm, 534 pm, 378 pm Q.7 267 pm, 231.2 pm, 188.8 pm
Q.8 3.5 g cm⁻³ Q.9 3.472 × 10²⁴ atoms Q.10 FCC
Q.11 0.24% Q.12 438.5 pm, 219.25 pm Q.13 6
Q.14 346.4 pm Q.15 19.4g/cm³, 143.9 pm Q.17 41.67 g cm⁻³
Q.18 5.74 g cm⁻³ Q.19 a = 5.94 × 10⁻⁸ cm, V = 2.096 × 10⁻²² cm³ Q.20 1.81 Å

PROFICIENCY TEST

1. F 2. T 3. T 4. T
5. F 6. T 7. T 8. F
9. T 10. T 11. $\sqrt{3} a = 4r$ 12. $\sqrt{2} a = 4r]$
13. cubic close, FCC 14. hexagonal close, HP
15. $c = 4r \sqrt{\frac{2}{3}}$ 16. least or minimum 17. 12
18. 0.732 19. $\frac{\sqrt{3}a}{2}$ 20. decreases, remains constant

EXERCISE II

- Q.1 123.84 pm Q.2 175.8 pm Q.3 AB₂O₄ Q.4 103.4 pm, No
Q.5 6.01 × 10²³ Q.6 4, 6, 8 Q.7 7.887 g/cc, 8.59 gm/cm³
Q.8 (a) 1.143, (b) 1.172
Q.9 5.188 gm/cm³, 6.023 × 10²² atoms of A, 3.0115 × 10²² unit cells
Q.11 2.16 gm/cm³ Q.12 3.57 Å Q.13 2.685 Å Q.14 15.053
Q.15 (a) octahedral, (b) 1/4 Q.16 4.34 Å
Q.17 6.02 × 10¹⁸ mol⁻¹ Q.18 0.414 r, 79.3%
Q.19 (a) MnF₃, (b) 6, (c) 4.02 Å Q.20 (a) 1.49 Å, (b) 1.37 g/cm³

Q.21 (a) 2.88 Å, (b) 12, (c) 19.4 g/cc

Q.22 4 molecules of H₂O

Q.23 for Fe is bcc, for V is bcc, for Pd is face centered

Q.24 (a) 4.5 Å, (b) 5.2 Å, (c) 8, (d) 6, (e) 0.92 g/cm³

Q.26 XY₃, 4.38 g/cm³

Q.27 (a) 3.52 Å, (b) 1.24 Å

Q.28 Mg₂SiO₄, Fe₂SiO₄, 59%

Q.29 (i) 3.90, (ii) 0.120 g/cc

Q.30 2.376%

EXERCISE III

Q.1 B Q.2 C Q.3 D Q.4 C Q.5 C Q.6 D Q.7 D

Q.8 C Q.9 A Q.10 B Q.11 B Q.12 A Q.13 B Q.14 C

Q.15 B Q.16 A Q.17 D Q.18 A Q.19 D Q.20 D

EXERCISE IV

Q.1 216.5 pm

Q.2 117.1 pm

Q.3 B

Q.4 (i) = 5 kg m⁻³

(ii) There is huge difference in theoretically calculated density and observed density. It is only possible if some foreign species occupies interstitial space i.e. substitution defect.

Q.5 Discuss

Q.6 A

Q.7 Discuss

Q.8 D

Q.9 True

Q.10 A

Q.11 1.259

Q.12 A, C, D

Q.13 12

Q.14 2.165 g/cm³

Q.15 (i) 124.27 pm, (ii) 7.30 g/cm³

STUDY PACKAGE

Target: IIT-JEE (Advanced)

SUBJECT: CHEMISTRY-XII

TOPIC: 14. Solutions

Index:

- 1. Key Concepts**
- 2. Exercise I**
- 3. Exercise II**
- 4. Exercise III**
- 5. Exercise IV**
- 6. Answer Key**
- 7. 34 Yrs. Que. from IIT-JEE**
- 8. 10 Yrs. Que. from AIEEE**

KEY CONCEPTS

Vapor Pressure. The pressure exerted by the vapors of a liquid which are in equilibrium with it at a given temperature.

Note: It depends only on temperature and on nature of the liquid. It does NOT depend on the surface area

Raoult's Law. The equilibrium vapor pressure of a volatile component is linearly proportional to the mole fraction of that component in liquid phase.

For non-volatile solutes :

or relative lowering of vapor pressure,

A more useful form is

$$P(\text{solution}) = x_{\text{solvent}} P^0$$

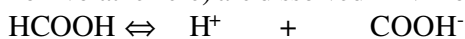
$$(P^0 - P)/P^0 = x_{\text{solute}}$$

$$(P^0 - P)/P = n/N$$

where n = total number of moles of *all the free solute species* in the solution *finally* (i.e. at equilibrium).

Three cases arise.

- (i) **Non-electrolyte** is dissolved e.g. glucose or urea. These molecules do not dissociate into ions. If 0.1 mol of urea is dissolved in 50 moles of water, then $n/N = 0.1/50$ simply.
- (ii) **Strong electrolyte** is dissolved e.g. NaCl, $\text{Ca}(\text{NO}_3)_2$ etc. These dissociate nearly completely into ions. If 0.1 mol of NaCl is dissolved in 50 moles of water, then $n/N = 0.2/50$ since NaCl dissociates completely into 0.1 mol Na^+ ions and 0.1 mol Cl^- ions. Similarly, for $\text{Ca}(\text{NO}_3)_2$, $n/N = 0.3/50$ if 0.1 mol of it dissociates completely into ions.
- (iii) **Weak electrolyte** is dissolved e.g. HCOOH , CH_3NH_2 etc. In such cases, we should determine the *total* number of moles of all the solute species at equilibrium. e.g. if n_0 moles of formic acid (considered non-volatile here) are dissolved in N moles of solvent then,



$$n_0(1-\alpha) \quad n_0\alpha \quad n_0\alpha$$

Total number of moles at equilibrium = $n_0(1 + \alpha)$. Hence, $n/N = n_0(1 + \alpha)/N$.

Note : This factor, $n(\text{at equilibrium})/n(\text{original})$ is referred to as **van't Hoff factor**.

Ideal Solutions. The solutions which obey Raoult's Law are called ideal solution. For ideality :

$$(i) \Delta H_{\text{mix}} = 0, \quad (ii) \Delta V_{\text{mix}} = 0 \text{ as well for liquid-liquid solutions.}$$

Non ideal solution (Deviations From Raoult's Law)

Positive deviation. When the observed vapor pressure is *more than* that expected by Raoult's law.

This is observed when $\Delta H_{\text{mix}} > 0$ i.e. energy is absorbed on mixing. Usually obtained by mixing of polar liquids with non-polar ones. e.g. cyclohexane and ethanol.

Negative deviation. When the observed vapor pressure is *less than* that expected by Raoult's law. This is observed when $\Delta H_{\text{mix}} < 0$ i.e. energy is released on mixing. Attractive forces between unlike molecules are greater than the forces of attraction between like molecules. e.g. chloroform and acetone. (Curve 3 in Fig. 1 and 2).

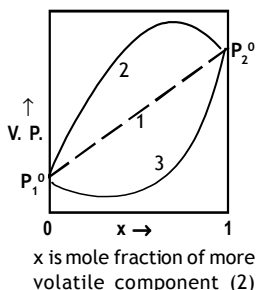


Fig. 1

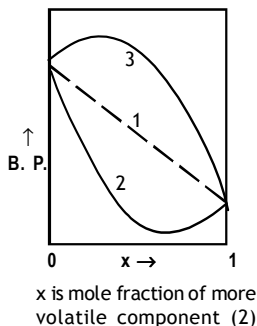


Fig. 2

Azeotropic Solutions. During distillation, the mole fraction of more volatile component in vapor state is higher than that in liquid state. This makes distillation possible. However, there exist some solutions for particular compositions of which the mole fraction of components in liquid and vapor state is same. Thus, no advantage is derived by distilling such a mixture and it is termed as **azeotropic**.

Completely Immiscible Liquids : When they are distilled, they distil in the ratio of their vapor pressure

at that temperature. e.g. When A and B are distilled wt ratio $\frac{w_B}{w_A}$ is given as $\frac{w_B}{w_A} = \frac{P_B^0 \cdot M_B}{P_A^0 \cdot M_A}$

Completely Miscible Liquids. They can be handled by Raoult's Law i.e.

$$y_i P = x_i P_i^0$$

where P = Total pressure of vapors in equilibrium with the liquid solution,

P_i^0 = vapor pressure of component i in pure state

y_i = mole fraction of i th component in vapor state, x_i = mole fraction of i th component in liquid state

This most fundamental expression may be arranged in many useful forms. e.g. for binary solutions :

$$P = x_1(P_1^0 - P_2^0) + P_2^0$$

or

$$1/P = 1/P_2^0 + y_1(1/P_1^0 - 1/P_2^0)$$

Note : Vapor pressure of an ideal solution is always between P_1^0 and P_2^0 (Curve 1 in Fig. 1 and 2)

Bubble Point. When the first bubble of vapor appears in liquid solution.

Dew Point. When the first drop of liquid condenses from a mixture of vapors. OR when the last drop of liquid remains and rest of the liquid is completely vaporised.

Colligative Properties. The properties which depend only on the number of moles of solute (and not on their molecular weights or sizes) are referred to as colligative properties.

e.g. Lowering of vapor pressure, depression of freezing point, elevation of boiling point, osmotic pressure etc.

1. **Relative lowering of vapour Pressure.**
$$\frac{P^0 - P}{P^0} = \frac{n}{n + N} = \frac{w/m}{w/m + W/M} = x_{\text{solute}}$$

2. **Elevation in Boiling Point, ΔT_b .** For dilute solutions, $\Delta T_b = K_b m$
 where m is molality of the solution (i.e. total number of moles of all the solute particles per kg of solvent).
 K_b is ebullioscopic or boiling point elevation constant which is given by

$$K_b = \frac{R(T_b^0)^2 M_{\text{solvent}}}{1000 \Delta H_{\text{vap}}}$$

ΔH_{vap} is the enthalpy of vaporisation of solvent.

3. **Depression in freezing Point (ΔT_f).** For dilute solutions, $\Delta T_f = K_f m$

where,

$$K_f = \frac{R(T_f^0)^2 M_{\text{solvent}}}{1000 \Delta H_{\text{fusion}}}$$

Osmosis. Spontaneous flow of solvent molecules through a semipermeable membrane from a pure solvent to the solution (or from a dilute solution to a concentrated solution) is termed as osmosis.

Reverse Osmosis. If a pressure greater than the osmotic pressure is applied on the concentrated solution, the solvent starts to flow from concentrated solution to dilute solution (or pure solvent). This is reverse osmosis. One of its chief uses is desalination of sea water to get pure drinking water.

4. **Osmotic Pressure (π).** The hydrostatic pressure built up on the solution which just stops osmosis. Alternately, it may be defined as the pressure which must be applied to the concentrated solution in order to stop osmosis.

For dilute solutions

$$\pi = cRT = h\rho g$$

where c is the total molar concentration of all the free species present in the solution, h is the height developed by the column of the concentrated solution and ρ is the density of the solution in the column. On the basis of osmotic pressure, the solutions can be classified in three classes.

Isotonic solutions. Two solutions having same osmotic pressures at same temperature. (This implies $c_1 = c_2$).

Hypertonic solution. When two solutions are being compared, then the solution with higher osmotic pressure is termed as hypertonic. The solution with lower osmotic pressure is termed as **hypotonic**.

Important. Osmotic pressures can be determined quite accurately, hence it is used in the determination of molecular weights of large proteins and similar substances.

Van't Hoff Factor (i)

Since colligative properties depends upon the number of particles of the solute, in some cases where the solute associates or dissociates in solution, abnormal results for molecules masses are obtained.

$$i = \frac{\text{Observed colligative property(actual)}}{\text{Theoretical colligative property}}$$

Liquid Solutions

- | | |
|--|---|
| 1. Vapour Pressure | Colligative properties (C.P.) |
| 2. Raoult's law | 1. Introduction |
| (i) When volatile solute is added | 2. The various C.P. |
| (a) When solute and solvent; both are miscible | (i) Lowering of V.P. |
| (b) When both are immiscible | (a) Determination of molar masses |
| (ii) When non-volatile solute is added. | (b) It's measurement |
| 3. Condensation of vapours of solution | (ii) Boiling point elevation |
| 4. Ideal and non-ideal solutions | (iii) Depression in freezing point |
| 5. Azeotropic mixtures | (iv) Osmotic pressure |
| | (a) Osmosis |
| | (b) Reverse osmosis |
| | (c) Isotonic solution |
| | 3. Van't Haff factor; Where the solute associates or dissociates in solution. |

EXERCISE I

Raoult's law

- Q.1 At 25°C, the vapour pressure of methyl alcohol is 96.0 torr. What is the mole fraction of CH₃OH in a solution in which the (partial) vapor pressure of CH₃OH is 23.0 torr at 25°C?
- Q.2 The vapour pressure of pure liquid solvent A is 0.80 atm. When a nonvolatile substance B is added to the solvent its vapour pressure drops to 0.60 atm. What is the mole fraction of component B in the solution?
- Q.3 The vapour pressure of pure water at 26°C is 25.21 torr. What is the vapour pressure of a solution which contains 20.0 glucose, C₆H₁₂O₆, in 70 g water?
- Q.4 The vapour pressure of pure water at 25°C is 23.76 torr. The vapour pressure of a solution containing 5.40 g of a nonvolatile substance in 90.0 g water is 23.32 torr. Compute the molecular weight of the solute.

Raoult's law in combinaton with Dalton's law of P.P. and V.P. lowering

- Q.5 The vapour pressure of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is prepared at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate total vapour pressure of the solution.
- Q.6 Calculate the mole fraction of toluene in the vapour phase which is in equilibrium with a solution of benzene and toluene having a mole fraction of toluene 0.50. The vapour pressure of pure benzene is 119 torr; that of toluene is 37 torr at the same temperature.
- Q.7 What is the composition of the vapour which is in equilibrium at 30°C with a benzene-toluene solution with a mole fraction of benzene of 0.40? With a mole fraction of benzene of 0.60?
 $P_b^\circ = 119 \text{ torr}$ and $P_t^\circ = 37 \text{ torr}$
- Q.8 At 90°C, the vapour pressure of toluene is 400 torr and that of σ -xylene is 150 torr. What is the composition of the liquid mixture that boils at 90°C, when the pressure is 0.50 atm? What is the composition of vapour produced?
- Q.9 Two liquids A and B form an ideal solution at temperature T. When the total vapour pressure above the solution is 400 torr, the mole fraction of A in the vapour phase is 0.40 and in the liquid phase 0.75. What are the vapour pressure of pure A and pure B at temperature T?
- Q.10 Calculate the relative lowering in vapour pressure if 100 g of a nonvolatile solute (mol.wt.100) are dissolved in 432 g water.
- Q.11 What weight of the 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 the solution?
- Q.12 The vapour pressure of an aqueous solution of glucose is 750 mm Hg at 373 K. Calculate molality and mole fraction of solute.

- Q.13 The vapour pressure of pure benzene at 25°C is 639.7 mm of Hg and the vapour pressure of a solution of a solute in C_6H_6 at the same temperature is 631.7 mm of Hg. Calculate molality of solution.
- Q.14 The vapour pressure of pure benzene at a certain temperature is 640 mm of Hg. A nonvolatile nonelectrolyte solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm of Hg. What is molecular weight of solid substance?
- Q.15 The vapour pressure of water is 17.54 mm Hg at 293 K. Calculate vapour pressure of 0.5 molal solution of a solute in it.
- Q.16 Benzene and toluene form two ideal solutions A and B at 313 K. Solution A (total pressure P_A) contains equal mole of toluene and benzene. Solution B contains equal masses of both (total pressure P_B). The vapour pressure of benzene and toluene are 160 and 60 mm Hg respectively at 313 K. Calculate the value of P_A/P_B .

Boiling point elevation and freezing point depression

- Q.17 When 10.6 g of a nonvolatile substance is dissolved in 740 g of ether, its boiling point is raised 0.284°C . What is the molecular weight of the substance? Molal boiling point constant for ether is $2.11^{\circ}\text{C}\cdot\text{kg/mol}$.
- Q.18 A solution containing 3.24 g of a nonvolatile nonelectrolyte and 200 g of water boils at 100.130°C at 1 atm. What is the molecular weight of the solute? (K_b for water 0.513°C/m)
- Q.19 The molecular weight of an organic compound is 58.0 g/mol. Compute the boiling point of a solution containing 24.0 g of the solute and 600 g of water, when the barometric pressure is such that pure water boils at 99.725°C .
- Q.20 An aqueous solution of a nonvolatile solute boils at 100.17°C . At what temperature will this solution freeze? [K_f for water 1.86°C/m]
- Q.21 Pure benzene freezes at 5.45°C . A solution containing 7.24 g of $\text{C}_2\text{H}_2\text{Cl}_4$ in 115.3 g of benzene was observed to freeze at 3.55°C . What is the molal freezing point constant of benzene?
- Q.22 A solution containing 6.35 g of a nonelectrolyte dissolved in 500 g of water freezes at -0.465°C . Determine the molecular weight of the solute.
- Q.23 The freezing point of a solution containing 2.40 g of a compound in 60.0 g of benzene is 0.10°C lower than that of pure benzene. What is the molecular weight of the compound? (K_f is 5.12°C/m for benzene)
- Q.24 The elements X and Y form compounds having molecular formula XY_2 and XY_4 . When dissolved in 20 gm of benzene, 1 gm XY_2 lowers the freezing point by 2.3° , whereas 1 gm of XY_4 lowers the freezing point by 1.3°C . The molal depression constant for benzene is 5.1. Calculate the atomic masses of X and Y.
- Q.25 Calculate the molal elevation constant, K_b for water and the boiling of 0.1 molal urea solution. Latent heat of vaporisation of water is $9.72 \text{ kcal mol}^{-1}$ at 373.15 K.
- Q.26 Calculate the amount of ice that will separate out of cooling a solution containing 50g of ethylene glycol in 200 g water to -9.3°C . (K_f for water = $1.86 \text{ K mol}^{-1} \text{ kg}$)

- Q.27 A solution of 0.643 g of an organic compound in 50 ml of benzene (density ; 0.879 g/ml) lowers its freezing point from 5.51°C to 5.03°C. If K_f for benzene is 5.12 K, calculate the molecular weight of the compound.
- Q.28 The cryoscopic constant for acetic acid is 3.6 K kg/mol. A solution of 1 g of a hydrocarbon in 100 g of acetic acid freezes at 16.14°C instead of the usual 16.60°C. The hydrocarbon contains 92.3% carbon. What is the molecular formula?

Osmotic pressure

- Q.29 Find the freezing point of a glucose solution whose osmotic pressure at 25°C is found to be 30 atm. $K_f(\text{water}) = 1.86 \text{ kg} \cdot \text{mol}^{-1} \cdot \text{K}$.
- Q.30 At 300 K, two solutions of glucose in water of concentration 0.01 M and 0.001 M are separated by semipermeable membrane. Pressure needs to be applied on which solution, to prevent osmosis? Calculate the magnitude of this applied pressure.
- Q.31 At 10°C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be 105.3 mm. Determine extent of dilution.
- Q.32 The osmotic pressure of blood is 7.65 atm at 37°C. How much glucose should be used per L for an intravenous injection that is to have the same osmotic pressure as blood?
- Q.33 What would be the osmotic pressure at 17°C of an aqueous solution containing 1.75 g of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) per 150 cm³ of solution?
- Q.34 A 250 mL water solution containing 48.0 g of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, at 300 K is separated from pure water by means of a semipermeable membrane. What pressure must be applied above the solution in order to just prevent osmosis?
- Q.35 A solution of crab hemocyanin, a pigmented protein extracted from crabs, was prepared by dissolving 0.750 g in 125 cm³ of an aqueous medium. At 4°C an osmotic pressure rise of 2.6 mm of the solution was observed. The solution had a density of 1.00 g/cm³. Determine the molecular weight of the protein.
- Q.36 The osmotic pressure of a solution of a synthetic polyisobutylene in benzene was determined at 25°C. A sample containing 0.20 g of solute/100 cm³ of solution developed a rise of 2.4 mm at osmotic equilibrium. The density of the solution was 0.88 g/cm³. What is the molecular weight of the polyisobutylene?
- Q.37 A 5% solution (w/v) of cane-sugar (Mol. weight = 342) is isotonic with 0.877% (w/v) of urea solution. Find molecular weight of urea.
- Q.38 10 gm of solute A and 20 gm of solute B are both dissolved in 500 ml water. The solution has the same osmotic pressure as 6.67 gm of A and 30 gm of B dissolved in the same amount of water at the same temperature. What is the ratio of molar masses of A and B?

Van't Hoff factor & colligative properties

- Q.39 A storage battery contains a solution of H_2SO_4 38% by weight. What will be the Van't Hoff factor if the $\Delta T_{f(\text{experiment})}$ is 29.08. [Given $K_f = 1.86 \text{ mol}^{-1} \text{ Kg}$]

- Q.40 A certain mass of a substance, when dissolved in 100 g C_6H_6 , lowers the freezing point by $1.28^\circ C$. The same mass of solute dissolved in 100g water lowers the freezing point by $1.40^\circ C$. If the substance has normal molecular weight in benzene and is completely ionized in water, into how many ions does it dissociate in water? K_f for H_2O and C_6H_6 are 1.86 and $5.12 K kg mol^{-1}$.
- Q.41 2.0 g of benzoic acid dissolved in 25.0g of benzene shows a depression in freezing point equal to $1.62 K$. Molal depression constant (K_p) of benzene is $4.9 K.kg.mol^{-1}$. What is the percentage association of the acid?
- Q.42 A decimolar solution of potassium ferrocyanide is 50% dissociated at 300K. Calculate the osmotic pressure of the solution. ($R=8.314 JK^{-1} mol^{-1}$)
- Q.43 The freezing point of a solution containing 0.2 g of acetic acid in 20.0g of benzene is lowered by $0.45^\circ C$. Calculate the degree of association of acetic acid in benzene. (K_f for benzene = $5.12 K mol^{-1} kg$)
- Q.44 0.85 % aqueous solution of $NaNO_3$ is apparently 90% dissociated at $27^\circ C$. Calculate its osmotic pressure. ($R= 0.082 l atm K^{-1} mol^{-1}$)
- Q.45 A 1.2% solution (w/v) of NaCl is isotonic with 7.2% solution (w/v) of glucose. Calculate degree of ionization and Van't Hoff factor of NaCl.

PROFICIENCY TEST

Q.1 Fill in the blanks with appropriate items :

1. Lowering of vapour pressure is _____ to the mole fraction of the solute.
2. The ratio of the value of any colligative property for NaCl solution to that of equimolal solution of sugar is nearly _____.
3. Semipermeable membrane allows the passage of _____ through it.
4. A binary solution which has same composition in liquid as well as vapour phase is called _____.
5. The molal elevation constant of solvent is also called _____.
6. The 0.1 M aqueous solution of acetic acid has boiling point _____ than that of 0.1 M aqueous solution of KCl.
7. For ideal solutions, the plot of total vapour pressure v/s composition is _____.
8. A solution of CHCl_3 and acetone shows _____ deviation.
9. Gases which react with water are generally _____ soluble in it.
10. Assuming complete dissociation, Van't Hoff's factor for Na_2SO_4 is equal to _____.
11. The osmotic pressure of a solution _____ with increase in temperature.
12. Water will boil at 101.5°C at pressure of _____ 76 cm of Hg.
13. Vant's Hoff's factor 'i' for dimerisation of CH_3COOH in benzene is _____.
14. $\pi = \frac{n_B}{V} RT$ is known as _____.
15. The molal elevation constant is the ratio of the elevation in boiling point to _____.

Q.2 True or False Statements :

16. Relative lowering of vapour pressure is a colligative property.
17. Lowering of vapour pressure of a solution is equal to the mole fraction of the non-volatile solute present in it.
18. The components of an azeotropic solution can be separated by simple distillation.
19. Vapour pressure of a liquid depends on the size of the vessel.
20. Addition of non-volatile solute to water always lowers its vapour pressure.
21. Reverse osmosis is generally used to make saline water fit for domestic use.
22. A 6% solution of NaCl should be isotonic with 6% solution of sucrose.
23. A real solution obeys Raoult's law.
24. Boiling point is a characteristic temperature at which vapour pressure of the liquid becomes higher than the atmospheric pressure.
25. Molal depression constant is independent of the nature of solute as well as that of solvent.
26. The real solutions can exhibit ideal behaviour at high concentrations.
27. The osmotic pressure decreases on addition of solvent to the solution.
28. For urea the value of Vant's Hoff's factor 'i' is equal to 1.
29. The unit of k_b is $\text{kg K}^{-1} \text{mol}^{-1}$.
30. 0.1 M solution of urea would be hypotonic with 0.1 M solution of NaCl.

EXERCISE II

- Q.1 An aqueous solution containing 288 gm of a non-volatile compound having the stoichiometric composition $C_xH_{2x}O_x$ in 90 gm water boils at 101.24°C at 1.00 atmospheric pressure. What is the molecular formula?
 $K_b(\text{H}_2\text{O}) = 0.512 \text{ K mol}^{-1} \text{ kg}$
 $T_b(\text{H}_2\text{O}) = 100^\circ\text{C}$
- Q.2 The degree of dissociation of $\text{Ca}(\text{NO}_3)_2$ in a dilute aqueous solution containing 7 gm of the salt per 100 gm of water at 100°C is 70%. If the vapour pressure of water at 100°C is 760 mm. Calculate the vapour pressure of the solution.
- Q.3 The addition of 3 gm of substance to 100 gm CCl_4 ($M = 154 \text{ gm mol}^{-1}$) raises the boiling point of CCl_4 by 0.60°C of $K_b(\text{CCl}_4)$ is $5.03 \text{ kg mol}^{-1} \text{ K}$. Calculate
- the freezing point depression
 - the relative lowering of vapour pressure
 - the osmotic pressure at 298 K
 - the molar mass of the substance
- Given $K_f(\text{CCl}_4) = 31.8 \text{ kg mol}^{-1} \text{ K}$ and ρ (density) of solution = 1.64 gm/cm^3
- Q.4 A 10% solution of cane sugar has undergone partial inversion according to the reaction:
 $\text{Sucrose} + \text{Water} \longrightarrow \text{Glucose} + \text{Fructose}$. If the boiling point of solution is 100.27°C .
- What is the average mass of the dissolved materials?
 - What fraction of the sugar has inverted? $K_b(\text{H}_2\text{O}) = 0.512 \text{ K mol}^{-1} \text{ kg}$
- Q.5 If 20 ml of ethanol (density = 0.7893 gm/ml) is mixed with 40 ml water (density = 0.9971 gm/ml) at 25°C , the final solution has density of 0.9571 gm/ml . Calculate the percentage change in total volume of mixing. Also calculate the molality of alcohol in the final solution.
- Q.6 Mixture of two liquids A and B is placed in cylinder containing piston. Piston is pulled out isothermally so that volume of liquid decreases but that of vapour increases. When negligibly small amount of liquid was remaining, the mole fraction of A in vapour is 0.4. Given $P_A^\circ = 0.4 \text{ atm}$ and $P_B^\circ = 1.2 \text{ atm}$ at the experimental temperature. Calculate the total pressure at which the liquid has almost evaporated. (Assume ideal behaviour).
- Q.7 1.5 g of a monobasic acid when dissolved in 150g of water lowers the freezing point by 0.165°C . 0.5 g of the same acid when titrated, after dissolution in water, requires 37.5 ml of N/10 alkali. Calculate the degree of dissociation of the acid (K_f for water = $1.86^\circ\text{C mol}^{-1}$).
- Q.8 Sea water is found to contain 5.85% NaCl and 9.50% MgCl_2 by weight of solution. Calculate its normal boiling point assuming 80% ionisation for NaCl and 50% ionisation of MgCl_2 [$K_b(\text{H}_2\text{O}) = 0.51 \text{ kg mol}^{-1} \text{ K}$].
- Q.9 The latent heat of fusion of ice is 80 calories per gram at 0°C . What is the freezing point of a solution of KCl in water containing 7.45 grams of solute in 500 grams of water, assuming that the salt is dissociated to the extent of 95%?
- Q.10 A complex is represented as $\text{CoCl}_3 \cdot x \text{NH}_3$. It's 0.1 molal solution in aq. solution shows $\Delta T_f = 0.558^\circ\text{C}$. K_f for H_2O is $1.86 \text{ K mol}^{-1} \text{ kg}$. Assuming 100% ionisation of complex and coordination no. of Co is six, calculate formula of complex.

- Q.11 The molar volume of liquid benzene (density = 0.877 g ml^{-1}) increases by a factor of 2750 as it vaporizes at 20°C and that of liquid toluene (density = 0.867 g ml^{-1}) increases by a factor of 7720 at 20°C has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution.
- Q.12 At 100°C , benzene & toluene have vapour pressure of 1375 & 558 Torr respectively. Assuming these two form an ideal binary solution, calculate the composition of the solution that boils at 1 atm & 100°C . What is the composition of vapour issuing at these conditions?
- Q.13 Calculate the boiling point of a solution containing 0.61 g of benzoic acid in 50 g of carbon disulphide assuming 84% dimerization of the acid. The boiling point and K_b of CS_2 are 46.2°C and $2.3 \text{ K kg mol}^{-1}$, respectively.
- Q.14 At 25°C , 1 mol of A having a vapor pressure of 100 torr and 1 mol of B having a vapor pressure of 300 torr were mixed. The vapor at equilibrium is removed, condensed and the condensate is heated back to 25°C . The vapors now formed are again removed, recondensed and analyzed. What is the mole fraction of A in this condensate?
- Q.15 Phenol associates in benzene to a certain extent to form a dimer. A solution containing $20 \times 10^{-3} \text{ kg}$ phenol in 1 kg of benzene has its freezing point depressed by 0.69 K. Calculate the fraction of phenol that has dimerised. K_f for benzene = $5.12 \text{ kg mol}^{-1}\text{K}$.
- Q.16 30 ml of CH_3OH ($d = 0.7980 \text{ g cm}^{-3}$) and 70 ml of H_2O ($d = 0.9984 \text{ g cm}^{-3}$) are mixed at 25°C to form a solution of density 0.9575 g cm^{-3} . Calculate the freezing point of the solution. $K_f(\text{H}_2\text{O})$ is $1.86 \text{ kg mol}^{-1} \text{ K}$. Also calculate its molarity.
- Q.17 Dry air was drawn through bulbs containing a solution of 40 grams of urea in 300 grams of water, then through bulbs containing pure water at the same temperature and finally through a tube in which pumice moistened with strong H_2SO_4 was kept. The water bulbs lost 0.0870 grams and the sulphuric acid tube gained 2.036 grams. Calculate the molecular weight of urea.
- Q.18 Vapour pressure of C_6H_6 and C_7H_8 mixture at 50°C is given by $P(\text{mm Hg}) = 180 X_B + 90$, where X_B is the mole fraction of C_6H_6 . A solution is prepared by mixing 936 g benzene and 736 g toluene and if the vapours over this solution are removed and condensed into liquid and again brought to the temperature of 50°C , what would be mole fraction of C_6H_6 in the vapour state?
- Q.19 When the mixture of two immiscible liquids (water and nitrobenzene) boils at 372 K and the vapour pressure at this temperature are 97.7 kPa (H_2O) and 3.6 kPa ($\text{C}_6\text{H}_5\text{NO}_2$). Calculate the weight % of nitrobenzene in the vapour.
- Q.20 The vapour pressure of a certain liquid is given by the equation:

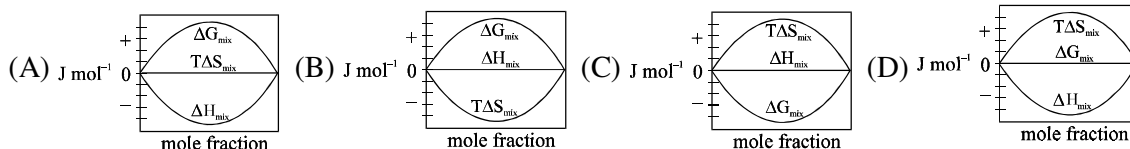
$$\log_{10} P = 3.54595 - \frac{313.7}{T} + 1.40655 \log_{10} T$$
 where P is the vapour pressure in mm and T = Kelvin Temperature. Determine the molar latent heat of vaporisation as a function of temperature. Calculate the its value at 80 K.
- Q.21 A very dilute saturated solution of a sparingly soluble salt A_3B_4 has a vapour pressure of 20 mm of Hg at temperature T, while pure water exerts a pressure of 20.0126 mm Hg at the same temperature. Calculate the solubility product constant of A_3B_4 at the same temperature.

- Q.22 The molar volume of liquid benzene (density = 0.877 g ml^{-1}) increases by a factor of 2750 as it vaporises at 20°C while in equilibrium with liquid benzene. At 27°C when a non-volatile solute (that does not dissociate) is dissolved in 54.6 cm^3 of benzene vapour pressure of this solution, is found to be 98.88 mm Hg . Calculate the freezing point of the solution.
 Given : *Enthalpy of vaporization of benzene(l)* = 394.57 J/gm
Molal depression constant for benzene = $5.0 \text{ K kg. mol}^{-1}$.
Freezing point of benzene = 278.5 K .
- Q.23 If the apparent degree of ionization of KCl ($\text{KCl} = 74.5 \text{ gm mol}^{-1}$) in water at 290 K is 0.86 . Calculate the mass of KCl which must be made up to 1 dm^3 of aqueous solution to the same osmotic pressure as the 4.0% solution of glucose at that temperature.
- Q.24 An ideal solution was prepared by dissolving some amount of cane sugar (non-volatile) in 0.9 moles of water. The solution was then cooled just below its freezing temperature (271 K), where some ice get separated out. The remaining aqueous solution registered a vapour pressure of 700 torr at 373 K . Calculate the mass of ice separated out, if the molar heat of fusion of water is 6 kJ .
- Q.25 The freezing point depression of a 0.109 M aq. solution of formic acid is -0.21°C . Calculate the equilibrium constant for the reaction,
 $\text{HCOOH (aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{HCOOH}^-(\text{aq})$
 K_f for water = $1.86 \text{ kg mol}^{-1} \text{ K}$
- Q.26 10 gm of NH_4Cl (mol. weight = 53.5) when dissolved in 1000 gm of water lowered the freezing point by 0.637°C . Calculate the degree of hydrolysis of the salt if its degree of dissociation of 0.75 . The molal depression constant of water is $1.86 \text{ kg mol}^{-1} \text{ K}$.
- Q.27 The freezing point of 0.02 mol fraction solution of acetic acid (A) in benzene (B) is 277.4 K . Acetic acid exists partly as a dimer $2\text{A} = \text{A}_2$. Calculate equilibrium constant for the dimerisation. Freezing point of benzene is 278.4 K and its heat of fusion ΔH_f is $10.042 \text{ kJ mol}^{-1}$.
- Q.28 A saturated solution of a sparingly soluble salt, MCl_2 has a vapour pressure of 31.78 mm of Hg at 30°C , while pure water exerts a pressure of 31.82 mm of Hg at the same temperature. Calculate the solubility product of the compound at this temperature.
- Q.29 The vapour pressure of two pure liquids, A and B that form an ideal solution are 300 and 800 torr respectively, at temperature T . A mixture of the vapour of A and B for which the mole fraction of A is 0.25 is slowly compressed at temperature T . Calculate
 (a) the composition of the first drop of the condensate,
 (b) the total pressure when this drop is formed,
 (c) the composition of the solution whose normal boiling point is T ,
 (d) the pressure when only the last bubble of vapour remains, and
 (e) the composition of the last bubble.
- Q.30 Tritium, T (an isotope of H) combines with fluorine to form weak acid TF , which ionizes to give T^+ . Tritium is radioactive and is a β -emitter. A freshly prepared aqueous solution of TF has pT (equivalent of pH) of 1.5 and freezes at -0.372°C . If 600 ml of freshly prepared solution were allowed to stand for 24.8 years. Calculate (i) ionization constant of TF . (ii) Number of β -particles emitted.
 (Given K_f for water = 1.86 mol K^{-1} , $t_{1/2}$ for tritium = 12.4 years)

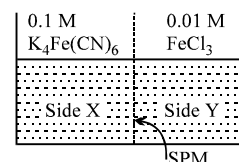
EXERCISE III

- Q.1 For an ideal binary liquid solution with $P_A^\circ > P_B^\circ$, which relation between X_A (mole fraction of A in liquid phase) and Y_A (mole fraction of A in vapour phase) is correct?
- (A) $Y_A < Y_B$ (B) $X_A > X_B$ (C) $\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$ (D) $\frac{Y_A}{Y_B} < \frac{X_A}{X_B}$
- Q.2 Mole fraction of A vapours above the solution in mixture of A and B ($X_A = 0.4$) will be
[Given : $P_A^\circ = 100$ mm Hg and $P_B^\circ = 200$ mm Hg]
- (A) 0.4 (B) 0.8 (C) 0.25 (D) none of these
- Q.3 The exact mathematical expression of Raoult's law is
- (A) $\frac{P^0 - P_s}{P^0} = \frac{n}{N}$ (B) $\frac{P^0 - P_s}{P^0} = \frac{N}{n}$ (C) $\frac{P^0 - P_s}{P_s} = \frac{n}{N}$ (D) $\frac{P^0 - P_s}{P^0} = n \times N$
- Q.4 A mixture contains 1 mole of volatile liquid A ($P_A^\circ = 100$ mm Hg) and 3 moles of volatile liquid B ($P_B^\circ = 80$ mm Hg). If solution behaves ideally, the total vapour pressure of the distillate is
- (A) 85 mm Hg (B) 85.88 mm Hg (C) 90 mm Hg (D) 92 mm Hg
- Q.5 Which of the following aqueous solution will show maximum vapour pressure at 300 K?
- (A) 1 M NaCl (B) 1 M CaCl_2 (C) 1 M AlCl_3 (D) 1 M $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
- Q.6 The Van't Hoff factor for a dilute aqueous solution of glucose is
- (A) zero (B) 1.0 (C) 1.5 (D) 2.0
- Q.7 The correct relationship between the boiling points of very dilute solution of AlCl_3 (T_1 K) and CaCl_2 (T_2 K) having the same molar concentration is
- (A) $T_1 = T_2$ (B) $T_1 > T_2$ (C) $T_2 > T_1$ (D) $T_2 \leq T_1$
- Q.8 A 0.001 molal solution of a complex $[\text{MA}_8]$ in water has the freezing point of -0.0054°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) $[\text{MA}_8]$ (B) $[\text{MA}_7]\text{A}$ (C) $[\text{MA}_6]\text{A}_2$ (D) $[\text{MA}_5]\text{A}_3$
- Q.9 The vapour pressure of a solution of a non-volatile electrolyte B in a solvent A is 95% of the vapour pressure of the solvent at the same temperature. If the molecular weight of the solvent is 0.3 times the molecular weight of solute, the weight ratio of the solvent and solute are
- (A) 0.15 (B) 5.7 (C) 0.2 (D) 4.0
- Q.10 At a given temperature, total vapour pressure in Torr of a mixture of volatile components A and B is given by
- $$P_{\text{Total}} = 120 - 75 X_B$$
- hence, vapour pressure of pure A and B respectively (in Torr) are
- (A) 120, 75 (B) 120, 195 (C) 120, 45 (D) 75, 45
- Q.11 Assuming each salt to be 90 % dissociated, which of the following will have highest boiling point?
- (A) Decimolar $\text{Al}_2(\text{SO}_4)_3$
(B) Decimolar BaCl_2
(C) Decimolar Na_2SO_4
(D) A solution obtained by mixing equal volumes of (B) and (C)

- Q.12 The vapour pressure of a solvent decreased by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be mole fraction of the solvent if decrease in vapour pressure is 20 mm of Hg
 (A) 0.2 (B) 0.4 (C) 0.6 (D) 0.8
- Q.13 Elevation of boiling point of 1 molar aqueous glucose solution (density = 1.2 g/ml) is
 (A) K_b (B) $1.20 K_b$ (C) $1.02 K_b$ (D) $0.98 K_b$
- Q.14 What will be the molecular weight of CaCl_2 determined in its aq. solution experimentally from depression of freezing point?
 (A) 111 (B) < 111 (C) > 111 (D) data insufficient
- Q.15 1.0 molal aqueous solution of an electrolyte A_2B_3 is 60% ionised. The boiling point of the solution at 1 atm is ($K_{b(\text{H}_2\text{O})} = 0.52 \text{ K kg mol}^{-1}$)
 (A) 274.76 K (B) 377 K (C) 376.4 K (D) 374.76 K
- Q.16 Which of the following plots represents an ideal binary mixture?
 (A) Plot of P_{total} v/s $1/X_B$ is linear (X_B = mole fraction of 'B' in liquid phase).
 (B) Plot of P_{total} v/s Y_A is linear (Y_B = mole fraction of 'A' in vapour phase)
 (C) Plot of $\frac{1}{P_{\text{total}}}$ v/s Y_A is linear
 (D) Plot of $\frac{1}{P_{\text{total}}}$ v/s Y_B is non linear
- Q.17 Pressure over ideal binary liquid mixture containing 10 moles each of liquid A and B is gradually decreased isothermally. If $P_A^0 = 200 \text{ mm Hg}$ and $P_B^0 = 100 \text{ mm Hg}$, find the pressure at which half of the liquid is converted into vapour.
 (A) 150 mm Hg (B) 166.5 mm Hg (C) 133 mm Hg (D) 141.4 mm Hg
- Q.18 The lowering of vapour pressure in a saturated aq. solution of salt AB is found to be 0.108 torr. If vapour pressure of pure solvent at the same temperature is 300 torr. Find the solubility product of salt AB
 (A) 10^{-8} (B) 10^{-6} (C) 10^{-4} (D) 10^{-5}
- Q.19 Which of the following represents correctly the changes in thermodynamic properties during the formation of 1 mol of an ideal binary solution.



- Q.20 FeCl_3 on reaction with $\text{K}_4[\text{Fe}(\text{CN})_6]$ in aqueous solution gives blue colour. These are separated by a semipermeable membrane AB as shown. Due to osmosis there is
 (A) blue colour formation in side X.
 (B) blue colour formation in side Y.
 (C) blue colour formation in both of the sides X and Y.
 (D) no blue colour formation.



EXERCISE IV

OBJECTIVE

- Q.1 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) 91.3% (B) 87% (C) 100% (D) 74% [JEE 1999]
- Q.2 In the depression of freezing point experiment, it is found that
(I) The vapour pressure of the solution is less than that of pure solvent.
(II) The vapour pressure of the solution is more than that of pure solvent.
(III) Only solute molecules solidify at the freezing point.
(IV) Only solvent molecules solidify at the freezing point.
(A) I, II (B) II, III (C) I, IV (D) I, II, III [JEE 1999]
- Q.3 During depression of freezing point in a solution, 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 [JEE 2003]
- Q.4 A 0.004 M solution of Na_2SO_4 is isotonic with a 0.010 M solution of glucose at same temperature. The apparent degree of dissociation of Na_2SO_4 is
(A) 25% (B) 50% (C) 75% (D) 85% [JEE 2004]
- Q.5 The elevation in boiling point, when 13.44 g of freshly prepared CuCl_2 are added to one kilogram of water, is [Some useful data, $K_b(\text{H}_2\text{O}) = 0.52 \text{ K kg mol}^{-1}$, mol. wt. of $\text{CuCl}_2 = 134.4 \text{ gm}$]
(A) 0.05 (B) 0.1 (C) 0.16 (D) 0.21 [JEE 2005]

SUBJECTIVE

- Q.6 A very small amount of a nonvolatile solute (that does not dissociate) is dissolved in 56.8 cm^3 of benzene (density 0.889 g cm^{-3}). At room temperature, vapour pressure of this solution is 98.88 mm Hg while that of benzene is 100 mm Hg. Find 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? [JEE 1997]
- Q.7 A solution of a nonvolatile solute in water freezes at -0.30°C . The vapor pressure of pure water at 298K is 23.51 mmHg and K_f for water is 1.86 degree/molal. Calculate the vapor pressure of this solution at 298K. [JEE 1998]
- Q.8 To 500 cm^3 of water, $3 \times 10^{-3} \text{ kg}$ 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 are $1.86 \text{ K kg}^{-1} \text{ mol}^{-1}$ and 0.997 g cm^{-3} respectively. [JEE 2000]
- Q.9 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 polymerising into a completely insoluble solid. The polymerisation follows first-order kinetics. After 100 minute, 0.525 mole of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation and ideal behaviour for the final solution. [JEE 2001]

Q.10 Match the boiling point with K_b for x, y and z, if molecular weight of x, y and z are same. [JEE 2003]

	b.pt.	K_b
x	100	0.68
y	27	0.53
z	253	0.98

Q.11 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 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?

[JEE 2004]

Q.12 72.5 g of phenol is dissolved in 1 kg of a solvent ($k_f = 14$) which leads to dimerization of phenol and freezing point is lowered by 7 kelvin. What percent of total phenol is present in dimeric form?

[JEE 2006]

ANSWER**EXERCISE I**

Q.1	0.24	Q.2	0.25	Q.3	24.5 torr	Q.4	57.24 g/mol
Q.5	66.13 mm Hg	Q.6	0.237	Q.7	0.682, 0.318; 0.829, 0.171		
Q.8	92 mol% toluene; 96.8 mol % toluene	Q.9	$P_A^\circ = 213.33 \text{ torr}$, $P_B^\circ = 960.0 \text{ torr}$				
Q.10	0.04	Q.11	111.1g, 18.52 molal	Q.12	0.741 m, 0.013		
Q.13	0.162 m	Q.14	65.25	Q.15	17.38	Q.16	0.964
Q.17	106 g/mol	Q.18	64.0 g/mol	Q.19	100.079°C	Q.20	- 0.62°C
Q.21	5.08°C/m	Q.22	50.8 g/mol	Q.23	2050 g/mol	Q.24	x = 25.6, y = 42.6
Q.25	$K_b = 0.512 \text{ kg mol K}^{-1}$, $T_b = 373.20 \text{ K}$	Q.26	38.71 g	Q.27	156.06		
Q.28	C_6H_6	Q.29	$T_f = -2.28^\circ\text{C}$	Q.30	$P = 0.2217 \text{ atm}$ should be applied		
Q.31	$(V_{\text{final}} = 5 \cdot V_{\text{original}})$	Q.32	54.2 g	Q.33	0.81 atm	Q.34	13.8 atm
Q.35	$5.4 \times 10^5 \text{ g/mol}$	Q.36	$2.4 \times 10^5 \text{ g/mol}$	Q.37	59.99		
Q.38	$M_A/M_B = 0.33$	Q.39	i = 2.5	Q.40	3 ions	Q.41	$\alpha = 99.2\%$
Q.42	$7.482 \times 10^5 \text{ Nm}^{-2}$	Q.43	94.5 %	Q.44	4.64 atm	Q.45	0.95; 1.95

PROFICIENCY TEST

1. proportional	2. 2 : 1	3. solvent molecules	4. azeotropic mixture
5. Ebullioscopic constant	6. lesser	7. straight line with slope $\neq 0$	
8. negative	9. more	10. 3	11. increases
12. greater than	13. less than 1		
14. Van't Hoff's solution equation	15. molality	16.	T
17. F	18. F	19. F	20. T
21. T	22. F	23. F	24. F
25. F	26. F	27. T	28. T
29. F	30. T		

EXERCISE II

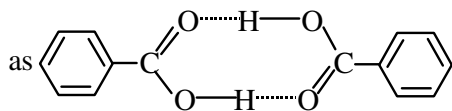
- Q.1 $C_{44}H_{88}O_{44}$ Q.2 746.24 mm/Hg
- Q.3 (a) 3.79°C, (b) 0.018, (c) 4.65 atm, (d) 251.5 Q.4 (a) 210, (b) 64.1%
- Q.5 % change in volume = 3.05, 8.604 m Q.6 0.66 atm Q.7 18.34%
- Q.8 $T_b = 102.3^\circ\text{C}$ Q.9 $T_f = -0.73^\circ\text{C}$ Q.10 $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ Q.11 0.73
- Q.12 $x_b = 0.2472$, $Y_b = 0.4473$ Q.13 46.33°C Q.14 $x_a'' = 0.1$
- Q.15 $\alpha = 0.7333$ Q.16 -19.91°C , 7.63 M Q.17 $M = 53.8$
- Q.18 0.93 Q.19 20.11 %
- Q.20 ΔH_v at 80 K is 1659.1 calorie; $\Delta H_v = R [2.303 \times 313.7 + 1.40655T]$
- Q.21 5.4×10^{-13} Q.22 $T_f = 277.5 \text{ K}$ Q.23 8.9 gm
- Q.24 12.54 Q.25 $K_a = 1.46 \times 10^{-4}$ Q.26 $h = 0.082$ Q.27 $K = 3.36$
- Q.28 $4.9 \times 10^{-5} \text{ M}^3$
- Q.29 (a) 0.47, (b) 565 torr, (c) $x_A = 0.08$, $x_B = 0.92$, (d) 675 torr, (e) $x'_A = 0.11$, $x'_B = 0.89$
- Q.30 (i) $K_a = 7.3 \times 10^{-3}$ (ii) 4.55×10^{22}

EXERCISE III

- Q.1 C Q.2 C Q.3 C Q.4 B Q.5 D Q.6 B Q.7 B
- Q.8 C Q.9 B Q.10 C Q.11 A Q.12 C Q.13 D Q.14 B
- Q.15 D Q.16 C Q.17 D Q.18 C Q.19 C Q.20 D

EXERCISE IV

- Q.1 B Q.2 C Q.3 A Q.4 C
- Q.5 C Q.6 0.1452, 5.028 K m^{-1}
- Q.7 23.44 mm Hg Q.8 0.229 Q.9 1.0×10^{-4}
- Q.10 $K_b(x) = 0.68$, $K_b(y) = 0.53$, $K_b(z) = 0.98$
- Q.11 (a) 122, (b) It means that benzoic acid remains as it is in acetone while it dimerises in benzene



- Q.12 35% phenol is present in dimeric form

STUDY PACKAGE

Target: IIT-JEE (Advanced)

SUBJECT: CHEMISTRY-XII

TOPIC: 15. Surface Chemistry

Index:

- 1. Key Concepts**
- 2. Exercise I**
- 3. Exercise II**
- 4. Exercise III**
- 5. Exercise IV**
- 6. Answer Key**
- 7. 34 Yrs. Que. from IIT-JEE**
- 8. 10 Yrs. Que. from AIEEE**

SURFACE CHEMISTRY

PHASE OF COLLOIDS :

A colloidal system is heterogeneous in character. It consists of two phases, namely a dispersed phase and a dispersion medium.

- (a) **Dispersed Phase** : It is the component present in small proportion and is just like a solute in a true solution. For example, in the colloidal state of sulphur in water, the former acts as a dispersed phase.
- (b) **Dispersion Medium** : It is normally the component present in excess and is just like a solvent in a solution.

The particles of the dispersed phase are scattered in the dispersion medium in a colloidal system.

CLASSIFICATION OF COLLOIDS :

Colloids can be classified in a number of ways based upon some of their important characteristics.

(1) **Physical state of Dispersed Phase & Dispersion Medium:**

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gaseous, eight types of colloidal system are possible. A gas mixed with another gas forms a homogeneous mixture and not a colloidal system. Typical examples of various type along with their characteristic names are given in table.

Common Colloidal System

<i>Dispersed Phase</i>	<i>Dispersion medium</i>	<i>Colloidal system</i>	<i>Examples</i>
Gas	Liquid	Foam or froth	Soap sols, lemonade froth, whipped cream.
Gas	Solid	Solid foam	Pumice stone, styrene, foam, foam rubber.
Liquid	Gas	Aerosols of Liquids	Fog, clouds, fine insecticide sprays.
Liquid	Liquid	Emulsions	Milk
Liquid	Solid	Gels	Cheese, butter, boot polish, table jellies.
Solid	Gas	Aerosols of Solid	Smoke, dust
Solid	Liquid	Sols	Must paint, starch dispersed in water, gold sol, muddy water, inks.
Solid	Solid	Solid sols	Ruby glass, some gem stones.

- * A colloidal system in which the dispersion medium is a liquid or gas are called sols. They are called hydrosols or aqua sols, if the dispersion medium is water. When the dispersion medium is alcohol or benzene, they are accordingly called alcosols or benzosol.
- * Colloidal systems in which the dispersion medium is a gas are called aerosols.
- * Colloids in which the dispersion medium is a solid are called gels, e.g. cheese etc. They have a more rigid structure. Some colloids, such as gelatin, can behave both as a sol and a gel. At high temperature and low concentration of gelatin, the colloid is a hydrosol. But at low temperature and high gelatin concentration, the hydrosol can change into a gel.

(2) **Based on interaction or affinity of phases :** On the basis of the affinity or interaction between the dispersed phase and the dispersion medium, the colloids may be classified into two types :

- (i) **Lyophilic Colloids :** The colloidal system in which the particle of dispersed phase have great affinity for the dispersion medium, are called lyophilic (solvent-loving) colloids. In such colloids, the dispersed phase does not get easily precipitated and the sols are more stable. Such colloidal systems, even if precipitated, may be reconverted to the colloidal state by simply agitating them with the dispersion medium. Hence lyophilic colloids are reversible. When the dispersion medium is water, these are called hydrophilic colloids. Some common examples of lyophilic colloids are gum, gelatin, starch, rubber, proteins, etc.
- (ii) **Lyophobic colloids :** The colloidal system in which the dispersed phase have no affinity for the dispersion medium are called lyophobic (solvent hating) colloids. They are easily precipitated (or coagulated) on the addition of small amounts of the electrolyte, by heating or by shaking. They are less stable and irreversible. When the dispersion medium is water, these are known as hydrophobic colloids. Examples of lyophobic colloids include sols of metals and their insoluble compounds like sulphides and oxides.

The essential differences between the lyophilic and lyophobic colloids are summarised in table.

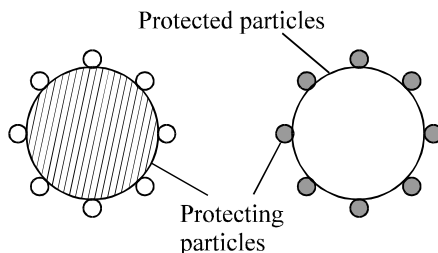
Difference between Lyophilic and Lyophobic sols

<i>Property</i>	<i>Lyophilic sols</i>	<i>Lyophobic sols</i>
1. Nature	Reversible	Irreversible
2. Preparation	They are prepared very easily by shaking or warming the substance with dispersion medium. They do not required any electrolyte for stabilization.	They are difficult to prepare, Special methods are used. Addition of stabiliser is essential for their stability.
3. Stability	They are very stable and are not easily coagulated by electrolytes.	They are generally unstable and get easily coagulated on addition of electrolytes.
4. Charge	Particles carry no or very little charge depending upon the pH of the medium.	Colloidal particles have characteristic charge (positive or negative)
5. Viscosity	Viscosity is much higher than that of the medium.	Viscosity is nearly the same as that of the medium
6. Surface Tension	Surface tension is usually less than that of the medium.	Surface tension is nearly the same as that of the medium.
7. 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.
8. Solvation	Particles are heavily solvated.	Particles are not solvated.
9. Visibility	The particles cannot be seen under ultra microscope.	The particles though invisible, can be seen under ultra microscope.
10. Tyndall effect	Less distinct.	More distinct.
11. Action of electrolyte	Large amount of electrolyte is required to cause coagulation.	Small amount of electrolyte is sufficient to cause cogulation.
12. Examples	Mostly organic substances e.g. starch, gums, proteins, gelatin etc.	Generally inorganic substance e.g., metal sols, sulphides and oxides sols.

* **PROTECTIVE COLLOIDS :**

Lyophilic sols are more stable than the lyophobic sols. This is because, lyophilic colloids are extensively hydrated and these hydrated particles do not combine to form large aggregates.

Lyophobic sols are more easily coagulated by the addition of suitable electrolyte. To avoid the precipitation of lyophobic sol. by the addition of electrolyte, some lyophilic colloid is added to it. Such lyophilic colloid is called protective colloid and the action of lyophilic colloid by the electrolytes is known as protective anion. The substances commonly used as protective colloids are gelatin, albumin, gum arabic, casein, starch, glue etc. A gold sol. containing a little gelatin as protective colloid needs a very large amount of sodium chloride to coagulate the sol.



Explanation : The particles of the protective colloid get adsorbed on the particles of the lyophobic colloid, thereby forming a protective layer around it (figure). The protective layer prevents the precipitating ions from coming in contact with the colloidal particles.

According to a recent view, the increase in stability of the lyophobic colloid is due to the mutual adsorption of the lyophilic and lyophobic colloids. It is immaterial which is adsorbed on which. In fact the smaller particles, whether of the protective colloid or the lyophobic colloid, are adsorbed on the bigger particles.

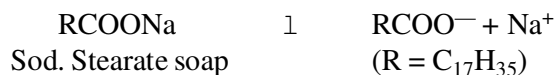
(3) **Based on type of particles of the dispersed phase :** Depending upon the molecular size, the colloidal system has been classified into three classes :

(i) **Multimolecular colloids :** The multimolecular colloidal particles consists of aggregate of atoms of small molecules with diameters less than 10^{-9} m or 1 nm.

For example, a sol. of gold contains particles of various sizes having several atoms. A sol. of sulphur consists of particles containing a thousand or so S_2 molecules. These particles are held together by vander Waal's forces. These are usually lyophobic sols.

(ii) **Macromolecular colloids :** The macromolecular colloidal particles themselves are large molecules. They have very high molecular weights varying from thousands to millions. These substances are generally polymers. Naturally occurring macromolecules are such as starch, cellulose and proteins. Artificial macromolecules are such as polyethylene, nylon, polystyrene, dacron, synthetic rubber, plastics, etc. The size of these molecules are comparable to those of colloidal particles and therefore, their dispersion known as macromolecular colloids. Their dispersion also resemble true solutions in some respects.

(iii) **The associated colloids or miscelles :** These colloids behave as normal electrolytes at low concentrations but colloids at higher concentrations. This is because at higher concentrations, they form aggregated (associated) particles called miscelles. Soap and synthetic detergents are examples of associated colloids. They furnish ions which may have colloidal dimensions.



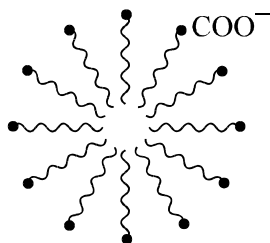
The long-chain RCOO^- ions associates or aggregate at higher concentrations and form miscelles and behave as colloids. They may contain 100 or more molecules.

Sodium stearate $\text{C}_{17}\text{H}_{35}\text{COONa}$ is an example of an associated colloid. In water it gives Na^+ and stearate, $\text{C}_{17}\text{H}_{35}\text{COO}^-$ ions. These ions associate to form miscelles of colloidal size.

Colloids which behave as normal electrolytes at low concentration, but exhibit colloidal properties at higher concentration due to the formation of aggregated particles called micelles are referred to as associated colloids. The micelles are formed by the association of dispersed particles above a certain concentration and certain minimum concentration is required for the process of aggregation to take place. The minimum concentration required for micelle formation is called micellisation concentration (CMC) and its value depends upon the nature of the dispersed phase. For soaps CMC is 10^{-3} mole L^{-1} .

Mechanism of Micelle Formation :

Micelles are formed by surface active molecules called surfactants such as soaps and detergents. These molecules have lyophilic group at one end and a lyophobic group at the other end. Let us take the example of a soap (say sodium oleate, $C_{17}H_{33}COO^-Na^+$). The long hydrocarbon part of oleate radical ($C_{17}H_{33}-$) is lyophobic end while COO^- part is lyophilic end. When the concentration of the solution is below its CMC, sodium oleate behaves as a normal electrolyte and ionises to give $C_{17}H_{33}COO^-$ and Na^+ ions. When the concentration exceeds CMC, the lyophobic part starts receding away from the solvent and tends to approach each other. However, the polar COO^- ends tend to interact with the solvent (water). This finally leads to the formation of bigger molecules having the dimensions of colloidal particles. Thus 100 or more oleate ions are grouped together in a spherical way keeping their hydrocarbon parts inside and the $-COO^-$ part remains projected in water.



PROPERTIES OF COLLOIDAL SOLUTIONS :

(1) 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 clearly indicate the heterogeneous character of colloidal system. Recent investigations however, shown that colloidal solutions are neither obviously homogeneous nor obviously heterogeneous.
- (ii) **Filterability :** Colloidal particles readily pass through ordinary filter papers. It is because the size of the pores of the filter paper is larger than that of the colloidal particles.
- (iii) **Non-settling nature :** Colloidal solutions are quite stable as the colloidal particles remain suspended in the dispersion medium indefinitely. Thus 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 :
 - (a) Size and shape of colloidal particles.
 - (b) Wavelength of the source of light.
 - (c) Method of preparation of the colloidal solution.
 - (d) Nature of the colloidal solution.
 - (e) The way an observer receives the light, i.e., whether by reflection or by transmission.
- (f) **Stability :** Colloidal solutions are quite stable. Only a few solutions of larger particles may settle but very slowly.

Examples :

- (i) Finest gold is red in colour. As the size of particles increases, it becomes purple.
- (ii) Dilute milk gives a bluish tinge in reflected light whereas reddish tinge in transmitted light.

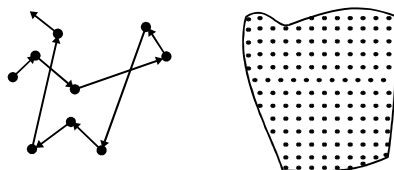
(2) **Mechanical Properties :**

- (a) **Brownian movement :** Colloids particles exhibit a ceaseless random and swarming motion. This kinetic activity of particles suspended in the liquid is called Brownina movement.

Robert Brown first observed this motion with pollen grains suspended in water.

Cause of movement : Brownian movement is due to bombardment of the dispersed particles by molecules of the medium. The Brownian movement (figure) depends upon the size of sol. particles. With the increase in the size of the particle, the chance of unequal bombardment decrease, and the Brownial movement too disappears. It is due to the fact that the suspension fails to exhibit this phe-nomenon.

It should be noted that Brownian movement does not change with time but changes with temperatures.



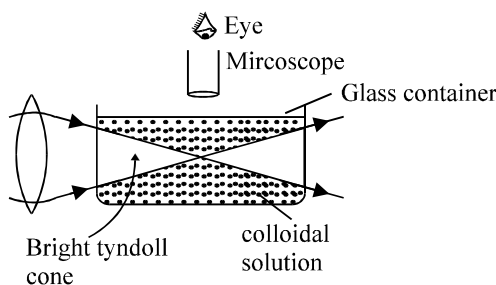
Importance :

- (i) Brownian movement is a direct demonstration of the assumption that the molecules in a gas or solution are in a state of constant ceaseless motion. Thus it confirms kinetic theory.
 - (ii) Brownian movement does not allow the colloidal particles to settle down due to gravity and thus is responsible for their stability.
 - (iii) Brownian movement helps to calculate the Avogadro's number (Detail beyond the scope of the book).
- (b) **Sedimentation :** Heavier sol. particle tend to settle down very slowly under the influence of gravity. This phenomenon is called sedimentation.

(3) **Optical Properties (Tyndal Effect) :**

When a strong and converging 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 (figure). This effect is called Tyndall effect. The light is observed as a bluish cone which is called Tyndall cone.

The Tyndall effect is due to scattering of light by the colloidal particles. The scattering of light cannot be due to simple reflection, because the size of the particles is smaller than the wave, length of the visible light and they are unable to reflect light waves. In fact, colloidal particles first absorb light and then a part of the absorbed light is scattered from the surface of the colloidal particles as a light of shorter wavelength. Since maximum scattering of light takes place at right angles to the place of incident light, it becomes visible when seen from that direction.



The Tyndall effect is observed under the following conditions :

- (i) The diameter of the dispersed particles must not be much smaller than the wavelength of light employed.
- (ii) The refractive indices of the dispersed phase and the dispersion medium must differ widely. This condition is fulfilled by lyophobic colloids.

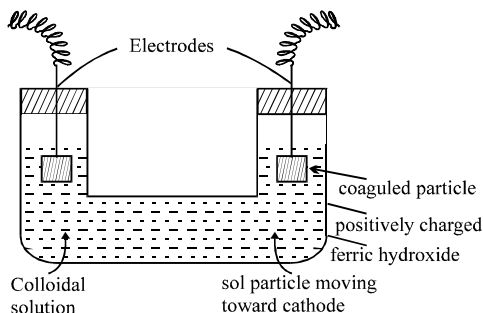
It is important to note that Tyndall effect is not shown by true solutions as their particles are too small to cause scattering. Tyndall effect has been used in devising ultramicroscope and in determining the number of colloidal particles in a colloidal solution.

(4) **Electrical Properties :**

The two electrical properties of colloidal solutions are :

- (a) **Electrophoresis or Cataphoresis** and (b) **Electro-osmosis**

- (a) **Electrophoresis or Cataphoresis :** In a colloidal solution, the colloidal particles are electrically charged and the dispersion medium has equal but opposite charge. Thus colloidal solution on the whole is electrically neutral. When an electric current is passed through a colloidal solution, the charged particles move towards the oppositely charged electrode where coagulate due to loss of charge.



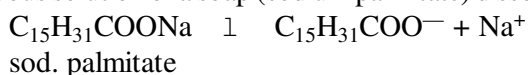
The phenomenon involving the migration of colloidal particles under the influence of electric field towards the oppositely charged electrode, is called electrophoresis or cataphoresis.

This phenomenon is used to determine the charge on the colloidal particles. For example, when a sol. of ferric hydroxide is taken in a U-tube and subjected to electric field, the ferric hydroxide (sol.) particles get accumulated near the cathode (figure). This shows that ferric hydroxide sol. particles are positively charged.

The sol. particles of metals and their sulphides are found to be negatively charged while those of metal hydroxides are positively charged. Basic dyes such as methylene blue haemoglobin are positively charged while acid dyes like are negatively charged.

Origin of charge : Various reasons have been given regarding the original of charge on the colloidal particles. These are given below :

- (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 a soap (sodium palmitate) dissociates into ions.



The 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 colloidal size bear negative charge.

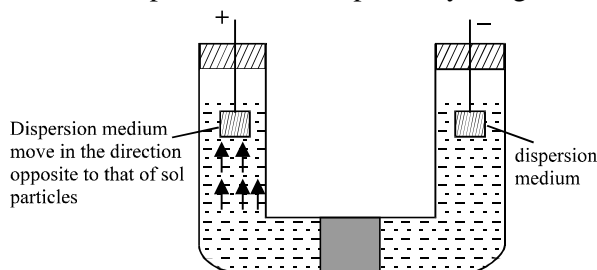
- (iii) **Preferential adsorption of ions from solution :** The charge on the colloidal particles is generally acquired by preferentially adsorbing positive or negative ions from the electrolyte. Thus AgCl particles can adsorb Cl^- ions from chloride solutions and Ag^+ ions; the sol. will be negatively charged in the first case and positively charged in the second case.
- (iv) **Capture of electron :** It is from air during preparation of sol. by Bredig's arc method.
- (v) **Dissociation of molecular electrolytes on the surface of particles :** H_2S molecules get adsorbed on sulphides during precipitation. By dissociation of H_2S , H^+ ions are lost and colloidal particles become negatively charged.

Electrical charged sols.

<i>Positively charged sols</i>	<i>Negatively charged sols</i>
1. Ferric hydroxide, aluminium hydroxide	Metals such as Pt, Au, Ag, Metals sulphides, e.g. arsenius sulphide.
2. Basic dyes such as methylene blue	Starch, clay, silicic acid.
3. Haemoglobin	Acid dyes, such as eosin.

- (b) **Electro-osmosis** : The phenomenon involving the migration of the dispersion medium and not the colloidal particles under the influence of an electric field is electro-osmosis.

Take the pure solvent (dispersion medium) in two limbs of U-tube. In the lower middle portion of U-tube, a porous diaphragm containing the colloidal system is present which divides the U-tube in two sections. In each section of U-tube, an electrode is present, as shown in figure. When the electrode potential is applied to the electrodes, the solid phase of sol. (colloidal system) cannot move but the solvent (dispersion medium) moves through the porous diaphragm towards one of the electrodes. The direction of migration of dispersion medium due to electro-osmosis determines the charge on sol. particles e.g., if the dispersion medium moves towards the cathode (negative electrode), the sol. particles are also negatively charged because the dispersion medium is positively charged as on the whole colloidal solution is neutral.



Electric double layer :

The surface of a colloidal particle acquires a positive or a negative charge by selective adsorption of ions carrying +ve or - ve charges respectively. The charged layer attracts counter ions from the medium which forms a second layer. Thus, an electrical double layer is formed on the surface of the particles i.e., one due to absorbed ions and the other due to oppositely charged ions forming a diffused layer. This layer consists of ion of both the signs, but its net charge is equal and opposite to those absorbed by the colloidal particles. The existence of charges of opposite signs on the fixed and diffused parts of the double layer creates a potential between these layers. This potential difference between the fixed charge layer and diffused layer of opposite charge is called electrokinetic potential or zeta potential.

- (c) **Coagulation** : 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 and hence precipitation will occur immediately.

This process by means of which the particles of the dispersed phase in a sol. are precipitated is known as *coagulation*.

If the coagulated particles instead of settling at the bottom of the container, float on the surface of the dispersion medium, the coagulation is called *flocculation*.

Most of the sols are coagulated by adding an electrolyte of opposite sign. This is due to the fact that the colloidal particles take up the ions of electrolyte whose charges are opposite to that on colloidal particles with the result that charge on the colloidal particles is neutralized. Thus coagulation takes place. For example, arsenius sulphide sol. (negatively charged) precipitated by adding barium chloride solution. It is due to the fact that the negatively charged particles of the sol. take up barium ions and get neutralized which lower the stability. As a result precipitation takes place.

It is observed that different amounts of different electrolytes is required to bring coagulation of a particular solution.

The minimum amount of an electrolyte required to cause precipitation of one litre 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*.

For example, the coagulation values of NaCl, BaCl₂ and AlCl₃ for arsenic sulphide sol. are 51, 0.69 and

0.093 millimoles/litre respectively. Thus their coagulating powers are $\frac{1}{51}$, $\frac{1}{0.69}$ and $\frac{1}{0.093}$ i.e., 0.0196, 1.449 and 10.75 respectively.

The coagulation values of a few electrolytes for negatively charged arsenic sulphide and positively charged ferric hydroxide sol. are given in table given below. The valency of the coagulation ion (the ion whose charge is opposite to that of the colloidal particles) is also give.

Coagulation values of different electrolytes

<i>Arsenic sulphide sol.</i>			<i>Ferric hydroxide sol.</i>		
Electrolyte	Valency of coagulating cation	coagulation value (millimoles/litre)	Electrolyte	Valency of coagulating cation	coagulation value (millimoles/litre)
K ₂ SO ₄	1	63	KBr	1	138
NaCl	1	51	KNO ₃	1	132
KNO ₃	1	50	KCl	1	103
MgSO ₄	2	0.81	K ₂ CrO ₄	2	0.320
BaCl ₂	2	0.69	K ₂ SO ₄	2	0.215
AlCl ₃	3	0.093	K ₃ Fe(Cn) ₆	3	0.096

From the above table, it is clear that the coagulating power of Al³⁺ ions in precipitating the arsenic sulphide sol. is approximately 550 times more than that of sodium (Na⁺) or potassium (K⁺) ions. Again, it is observed that the negatively charged arsenic sulphide sol. is coagulated by cations while positively charged ferric hydroxide sol. is coagulated by anions.

Hardy-Schulz rules : H. Schulze (1882) and W.B. Hardy (1900) suggested the following rules to discuss the effect of electrolytes of the coagulation of the sol.

- (1) Only the ions carrying charge opposite to the one present on the sol. particles are effective to cause coagulation, e.g., the negative charged sol. is best coagulated by cations and a positive sol. is coagulated by anions.
- (2) The charge on coagulating ion influences the coagulation of sol.

In general, the coagulating power of the active ion increases with the valency of the active ion. After observing the regularities concerning the sing and valency of the active ion, a law was proposed by Hardy and Schulz which is termed as Hardy-Schulze law which is stated as follows: "*Higher is the valency of the active ion, greater will be its power to precipitate the sol.*"

Thus, coagulating power of cations is in the order of Al³⁺ > Ba²⁺ or Mg²⁺ > Na⁺ or K⁺.

Similarly, to coagulating the positively charged sol. the coagulating power of anion is in the order of [Fe(CN)₆]⁴⁻ > PO₄³⁻ > SO₄²⁻ > Cl⁻

Some other methods of coagulation :

Apart from the addition of electrolyte, coagulation can also be carried out by following methods:

- (i) **By persistent dialysis** : It has been observed that traces of electrolytes are associated with the solution due to which it is stable. If the solution is subjected to prolonged dialysis, the traces of electrolytes are removed and coagulation takes place.

- (ii) **By mutual coagulation of colloids :** When two sols of oppositely charges are mixed together in a suitable proportion, the coagulation takes place. The charge of one is neutralized by the other. For example, when negatively charged arsenic sulphide sol. is added to positively charged ferric hydroxide sol., the precipitation of both occurs simultaneously.
- (iii) **By electrical method :** If the electrical charge of lyophobic sol. is removed by applying any electric field such as in electrophoresis, they also precipitate out.
- (iv) By excessive cooling or by excessive heating.
- (5) **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. But the effect of colloidal particles on colligative properties except osmotic pressure is very small. This is due to the large size of colloidal particles. The number of colloidal particles produced by a given mass of colloid is much less than the number produced in a molecular solution, containing the same mass of solute. Hence the colligative effect in colloidal solutions is too less.

Isoelectric Point of Colloid :

The hydrogen ion concentration at which the colloidal particles are neither positively charged nor negatively charged (i.e. uncharged) is known as isoelectric point of the colloid. At this point lyophilic colloid is expected to have minimum stability because at this point particles have no charge. The isoelectric point of gelatin is 4.7. This indicates that at pH = 4.7, gelating has no electrophoretic motion. Below 4.7, it moves towards the cathode and above 4.7 it moves forwards the anode. It is not always true, e.g., silicic acid has been found to have maximum stability at the isoelectric point.

EMULSIONS :

An emulsion is a colloidal solution of a liquid. It may be defined as a heterogeneous system consisting of more than one immiscible liquids dispersed in one another in the form of droplets whose diameter, in general, exceeds 0.1 μ .

For example, milk is an emulsion in which small drops of liquid fat are dispersed in aqueous medium. Cod liver oil is an emulsion in which the water drops are dispersed in the oil. This means in most of the emulsions one of the liquid is water and the other liquid is oil. Here the term 'oil' is used to represent all organic substances which are soluble in water.

The emulsion are classified as :

- (1) **Oil in water type emulsion (O/W):** In this emulsion, oil is the dispersed phase and water is the dispersion medium. It is denoted by O/W or O in W. For example, milk (liquid fat dispersed in water), vanishing cream, etc.
- (2) **Water in oil type :** In this emulsion, water is the dispersed phase and oil is the dispersion medium. It is denoted by W/O or W in O. For example, butter, cod liver oil, cold cream, etc.

The type of emulsion obtained by agitating two immiscible liquids depends upon the relative amounts of two components liquids. The liquid that is in excess forms the dispersion medium. Thus, the two types of emulsions can be interconverted into each other by changing the concentration of one of the liquids.

Distinction between two types of emulsions : the two types of emulsions may be distinguished from each other in a number of ways.

- (1) **Dye test :** It involves the addition of oil soluble dye to the emulsion under experiment. If the emulsion acquires the colour of the dye readily, it is water-in-oil type emulsion and if the emulsion remains colourless, it is oil-in-water type emulsion.
- (2) **Conductivity test :** It involves the addition of electrolyte to the emulsion under experiment. If the conductivity of the emulsion increases appreciably with the addition of electrolyte, it is oil-in-water type emulsion and if conductivity is very small, it is water-in-oil type emulsion.
- (3) **Dilution test :** As a general rule, an emulsion can be diluted with the dispersion medium while the addition of the dispersed phase forms a separate layer. Thus, if an emulsion can be diluted with oil, it is water-in-oil type.

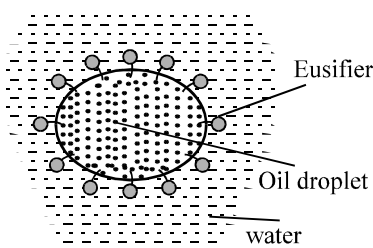
Preparation of emulsion (Emulsification) : Emulsification is the process which involves the preparation of emulsion. Generally, an emulsion is prepared by subjecting a mixture of the immiscible liquid to a distinct layers upon standing. The oil globules rise to form an upper layer while aqueous medium forms lower layers. To prevent the separation of layers and to get the stable emulsion, a small quantity of the third substance is added. This substance which stabilizes the emulsion is called *emulsifier* or *emulsifying agent*. The commonly used emulsifying agents are soaps, detergents and lyophilic colloids. Casein, a lyophilic colloid present in milk, acts as an emulsifier as it forms a protective layer around fat molecules dispersed in water. Hence milk is a fairly stable emulsion.

Function of emulsifier : The main function of emulsifier or emulsifying agents is to lower the interfacial tension between oil and water and thus helps the intermixing of two liquids. For example, a molecule of a soap or detergent (emulsifier) gets concentrated at the interface between oil and water. The polar end of the emulsifier is in water and non-polar end is in oil as shown in figure.

In a soap, RCOONa , R is the non-polar end, whereas $\text{COO}^- \text{Na}^+$ is the polar end.

Properties of emulsion :

- (i) The size of particles of the dispersed phase of an emulsion is usually larger than in sols.
- (ii) Like colloidal particles, emulsions exhibit properties such as Tyndall effect, Brownian movement (provided the particles are not too large), electrophoresis, coagulation, etc.



Demulsification : The process which involves the breaking of an emulsion into two separate liquid layers is called demulsification. The following methods may be used to bring demulsification:

- (1) **Chemical Methods :** An emulsion may be demulsified by adding a chemical substance whose action on the dispersed phase and the dispersion medium is opposite to that of the original emulsifying agent used to produce the stable emulsion.
- (2) **Centrifugation :** Cream is separated from milk by the centrifugal method.
- (3) **Cooling :** Fat can be removed from milk by keeping it in a refrigerator for a few hours.

Demulsification :

Besides the above noted methods of demulsification, the following methods have also been developed :

- (i) Suitable centrifugal action-milk cream is separated from milk by centrifugation.
- (ii) Application of electric field-electrophoresis.
- (iii) Addition of an electrolyte having multivalent opposite charge than that on the dispersed phase.
- (iv) Chemical destruction of stabiliser.
- (v) Distilling off of one of the components, usually water.
- (vi) Addition of demulsifiers like alcohol, phenol etc.

Oil in water type emulsion (O/W)

Use of emulsion :

- (1) 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.
- (2) All paints are emulsions.
- (3) 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.

- (4) Soaps and detergents remove dust and dirt from the dirty piece of cloth by making an oil in water emulsion.
- (5) Milk is an emulsion of liquid fats in water.
- (6) In the process of metallurgy, one of the important steps is the concentration of ore which is usually done by froth floatation process in which an oil is added to the finely-divided ore taken in water. The particles of ore go on the surface due to formation of foams while the other impurities are left at the bottom of the vessel.
- (7) The emulsion of asphalt in water is used in road making and building.

GELS :

Colloidal system in which liquids are the dispersed phase and solid act as the dispersion medium are called gels. The common examples are : boot polishes, jelly, gum arabic, agar agar, processed cheese and silicic acid.

When the gels are allowed to stand for a long time, they give out small quantities of trapped liquids with accumulate on its surface. This action of gels is known as Synresis or Weeping. Some gels such as silica, gelatin and ferric hydroxide liquify on shaking and reset on allowing to stand. This phenomenon of Sol-gel transformation is called thixotropy.

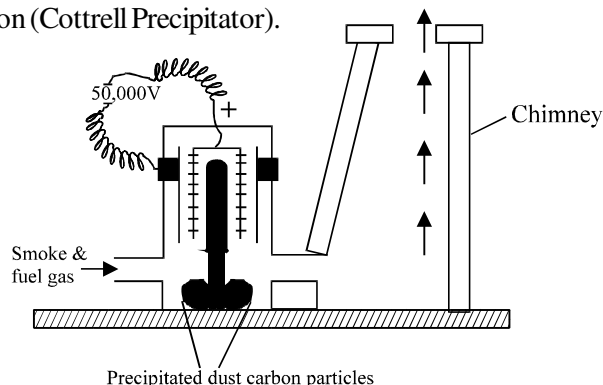
Gels are divided into two categories i.e. elastic gels and non elastic gels. The two categories differ from their behaviour towards dehydration and rehydration as under.

<i>Elastic gels</i>	<i>Non-elastic gels</i>
<ol style="list-style-type: none"> 1. They change to solid mass on dehydration which can be changed back to original form by addition of water followed by warming. 2. They absorb water when placed in it with simultaneous swelling. This phenomenon is called imbibation. 	<ol style="list-style-type: none"> 1. They change to solid mass on dehydration which cannot be changed back to original form with water. 2. They do not exhibit imbibation.

USES OF COLLOIDS :

- (1) **Medicines** : The medicines containing gold, silver or calcium etc. in colloidal form are more effective and easily assimilated by the human systems.
- (2) **Dyes** : In dyeing, mordants colloidal substances are used in textile dyeing industry to fasten dyes.
- (3) **Rubber industry** : Latex is a colloidal solution of negatively charged particles. The article to be rubber plated is made the anode. Under the influence of electric field the rubber particles get deposited on the anode and the article gets rubber plated.
- (4) **Smoke screens** : Smoke screens which consist of titanium dioxide dispersed in air are used in warfare for the purpose of concealment and camouflage.
- (5) **Formation of delta** : The river waver carries with it charged clay particles and many other substances in the form of colloidal solution. When the sea water comes in contact with these particles, the colloidal particles in river water are coagulated by the electrolytes present in sea water to form deltas.
- (6) **Purification of water** : The turbidity in water is due to the presence of negatively charged clay particles. The addition of potash alum, i.e., Al^{3+} ions neutralizes the negative charge on the colloidal particles and thus causes their coagulation. The coagulated matter settles down and thus becomes clear.
- (7) **Artificial rain** : Artificial rain can be caused by throwing electrified sand on clouds which are colloidal solutions or charged particles of water in air.

- (8) **Smoke precipitation** : Smoke coming out of the chimney in industrial area is a nuisance and health hazard. It is a colloidal particles are charged particles and thus they are removed from fuel gases by electrical precipitation (Cottrell Precipitator).



In cottrell precipitator, the smoke is made to pass through chambers fitted with highly electrically charged plates which precipitate the carbon and dust particles leaving in the gases to escape through chimney (figure).

- (9) **Sewage disposal** : Sewage water consists of particles of dirt, rubbish, mud, etc., which are of colloidal dimensions and carry an electric charge and thus do not settle down easily. These particles can thus be removed by cataphoresis. A system of two tanks fitted with metallic electrodes is used for this purpose. When electric field is created, then the dust particles are coagulated on he oppositely charged electrodes. The deposit may be utilized as a manure.
- (10) **Cleansing action of soap and detergent** : Soap solution may be used to wash off the dirt sticking to the fabric, in the presence
- If forms a collodial solution in water forms (miscelles), removes dirt by simple adsorption of oily substance and thus washes away.
 - It decreases the interfacial tension between water and grease, and it causes the emulsification of grease in water. By mechanical action such as rubbing, the dirt particles are also detached alongwith the only material.
- (11) **In Photography** : Various colloidal system are used in photographic process. In the preparation of photographic plates, the silver bromide in gelatin is coated on thin glass plates. In developing and fixation, various colloidal substances are used. In different kinds of colour printing, gelatin and other colloidal mixtures are used.
- (12) **Blue colour of the sky** : Colloidal particles scatter only blue light and the rest of is absorbed. In sky there are a number of dust and water particles. They scatter blue light and, therefore, sky looks bluish. If there were no scattering, the sky would have appeared totally dark.

SUMMARY OF COLLOIDAL STATE :

- Thomas Graham classified the substances into two categories on the basis of their diffusion through parchment membrane namely (i) Colloids (ii) Crystalloids.
- It has been realised that colloid is not a substance but it is a state of a substance which depends upon the molecular size.
- When the size of the particles is between 10^{-9} m (1nm) 10^{-7} m (100 nm), it behaves like colloid.
- In true solutions, the particle size is less than 1 nm and in suspensions, the particle size is more than 100 nm.
- The colloidal solutions in which there is no affinity between particles of the dispersed phase and the dispersion medium are called Iyophobic colloids or irreversible colloids.
- Associated colloids are the substances which behave as normal electrolytes at low concentration but behave as colloidal particles at higher concentration. For example, soap i.e. sod. stearate.

- (7) Lyophobic colloids are prepared by mainly three types of method
 - (i) Condensation methods
 - (ii) Dispersions method
 - (iii) Peptisation
- (8) The process of converting a freshly prepared precipitate into colloidal form by the addition of a suitable electrolyte is called peptisation.
- (9) The process of separating the particles of colloids from those of crystalloids by means of diffusion through a suitable membrane is called dialysis.
- (10) The process of dialysis i.e., separation of crystalloids from colloids is quickened by passing electric current through two electrodes suspended around the parchment bag. This process is called electrodialysis.
- (11) Ultra filtration is a process of removing the impurities from the colloidal solution by passing it through graded filter papers called ultra-filter papers.
- (12) The continuous zig-zag movement of the colloidal particles in a colloidal solutions is called Brownian movement. It is due to the collisions of dispersion medium particles with dispersed phase particles.
- (13) The process of scattering of light by the colloidal particles as a result of which the path of the beam becomes visible is called Tyndall effect.
- (14) The presence of electric charge either (positive or negative) on colloidal particles is responsible for the stability of colloidal solutions.
- (15) The phenomenon of movement of colloidal particles under the influence of electric field is called electrophoresis or cataphoresis.
- (16) A phenomenon in which the molecules of the dispersion medium are allowed to move under the influence of an electric current, whereas colloidal particles are not allowed to move, is called Electro-osmosis.
- (17) The phenomenon of precipitation of a colloidal solution by the addition of excess of an electrolyte is called coagulation or flocculation.
- (18) According to Hardy Schulze rule :
 - (i) The ions carrying the charge opposite to that of sol particles are effective in causing coagulation of the sol.
 - (ii) Coagulation power of an electrolyte is directly proportional to the valency of the active ions (ions causing coagulation).
- (19) The minimum concentration of an electrolyte which is required to cause the coagulation or flocculation of a sol. is known as flocculation value. It is usually expressed as millimoles per litre. The coagulating power of an electrolyte is inversely related to its coagulating value.
- (20) Gold number of a protective colloid is a minimum weight of it in milligrams which must be added to 10 ml of a standard red gold sol so that no coagulation of the gold sol. (i.e. change of colour from red to blue) takes place when 1 ml of 10 % sodium chloride solution is rapidly added to it. Obviously, smaller the gold number of a protective colloid, the greater is the protective action.

ADSORPTION :

- (1) Molecules at the surface of a solid, a metal, or a liquid experience in net inward force of attraction with free valencies.
- (2) The phenomenon of attracting and retaining the molecules of a substance on the surface of a solid or a liquid resulting in the higher concentration of the molecules on the surface is called adsorption.
- (3) The substance adsorbed on the surface is called adsorbate and the substance on which it is adsorbed is called adsorbent.
- (4) The reverse process i.e. removal of adsorbed substance from the surface is called desorption.
- (5) The adsorption of gases on the surface of metals is called occlusion.

- (6) The term sorption is employed when adsorption as well as absorption take place simultaneously.
- (7) Adsorption is a surface phenomenon, whereas absorption is a bulk phenomenon. Adsorption occurs only at the surface of adsorbent, whereas absorption occurs throughout the body of the material.
- (8) When the concentration of the adsorbate is more on the surface of the adsorbent than in the bulk, it is called positive adsorption.
- (9) When the concentration of the adsorbate is less relative to its concentration in the bulk, it is called negative adsorption.
- (10) When a gas is adsorbed at the surface of a solid by weak forces (Vander Waal's forces), it is called physical adsorption.
- (11) When a gas is held on the surface of a solid by forces similar to those of a chemical bond, it is called chemical adsorption or chemisorption.
- (12) Adsorption is accompanied by evolution of heat. The amount of heat evolved when one mole of a gas is adsorbed on a solid, is known as molar heat of adsorption. Its magnitude depends upon the nature of the gas.
- (13) The magnitude of gaseous adsorption depends upon temperature, pressure, nature of the gas and the nature of the adsorbent.
- (14) Adsorption decreases with increase in temperature, since it is accompanied by evolution of heat.
- (15) The adsorption increases with increase in pressure, since adsorption of gas leads to decrease in pressure.
- (16) The variation of adsorption with pressure at a constant temperature is called isotherm.
- (17) At low pressure, the amount of the gas adsorbed per unit quantity of adsorbent is proportional to the pressure. At high pressure, the amount of adsorbed gas is independent of pressure. At intermediate pressures, Freundlich adsorption isotherm is expected to hold.
- (18) More readily soluble and easily liquefiable gases HCl , Cl_2 , SO_2 and NH_3 are adsorbed more than the so called permanent gases such as H_2 , O_2 , N_2 etc. because Vander Waal's forces involved in adsorption are much predominant in the former gases than the latter category of gases.

PROFICIENCY TEST

Q.1 Fill in the blanks with appropriate items:

1. The substance on whose surface adsorption takes place is called an _____.
2. Removal of adsorbate from the surface of adsorbent is called _____.
3. Migration of colloidal particles under the effect of electric field is called _____.
4. The heat of adsorption in case of physisorption is approximately _____.
5. The phenomenon of zig-zag motion of colloidal particles is known as _____.
6. Lyophilic sols are _____ stable than lyophobic sols.
7. Electrical properties of a colloidal solution are demonstrated by _____.
8. Tyndall effect takes place due to _____ of light by colloidal particles.
9. The liquid-liquid colloidal dispersions are called _____.
10. The movement of dispersion medium under the influence of an electric field is called _____.
11. Smoke is a colloidal solution of _____ in _____.
12. The adhering of the molecules of a gas on the surface of a solid is called _____.
13. The protective action of different colloids is compared in terms of _____.
14. The colloidal dispersion of a liquid in a liquid is called _____.
15. The colloidal dispersions of liquids in solid media are called _____.

Q.2 True/False statements

1. Physisorption is non-specific.
2. Chemisorption needs activation energy.
3. A graph of x/m vs temperature at constant pressure is called adsorption isotherm.
4. Suspensions have solute particles with size less than 1 nm.
5. $\text{Fe}(\text{OH})_3$ sol contains positively charged colloidal particles.
6. Chemisorption is irreversible.
7. Adsorption isobars of chemisorption and physisorption are of the same type.
8. Milk is an example of water in oil emulsions.
9. Gold sol can be prepared by Bredig's arc method.
10. Gel is a system in which liquid is the dispersed phase and solid is the dispersion medium.

Select the correct alternative. (Only one is correct)

- Q.1 Which gas will be adsorbed on a solid to greater extent.
 (A) A gas having non polar molecule
 (B) A gas having highest critical temperature (T_c)
 (C) A gas having lowest critical temperature.
 (D) A gas having highest critical pressure.
- Q.2 Which of the following factors affects the adsorption of a gas on solid?
 (A) T_c (critical temp.) (B) Temperature of gas (C) Pressure of gas (D) All of them
- Q.3 The volume of gases NH_3 , CO_2 and CH_4 adsorbed by one gram of charcoal at 298 K are in
 (A) $\text{CH}_4 > \text{CO}_2 > \text{NH}_3$ (B) $\text{NH}_3 > \text{CH}_4 > \text{CO}_2$
 (C) $\text{NH}_3 > \text{CO}_2 > \text{CH}_4$ (D) $\text{CO}_2 > \text{NH}_3 > \text{CH}_4$
- Q.4 The heat of physisorption lie in the range of
 (A) $1 - 10 \text{ kJ mol}^{-1}$ (B) $20 \text{ to } 40 \text{ kJ mol}^{-1}$ (C) $40 \text{ to } 200 \text{ kJ mol}^{-1}$ (D) $200 \text{ to } 400 \text{ kJ mol}^{-1}$
- Q.5 Which of the following is not a gel?
 (A) Cheese (B) Jellies (C) Curd (D) Milk
- Q.6 Which of the following is used to adsorb water
 (A) Silica gel (B) Calcium acetate (C) Hair gel (D) Cheese
- Q.7 An emulsion is a colloidal system of
 (A) two solids (B) two liquids
 (C) one gas and one solid (D) one gas and one liquid
- Q.8 Which of the following is a lyophobic colloid?
 (A) Gelatin (B) Sulphur (C) Starch (D) Gum arabic
- Q.9 The nature of bonding forces in adsorption are
 (A) purely physical such as Van Der Waal's forces
 (B) purely chemical
 (C) both chemical and physical
 (D) sometimes physical and sometimes chemical
- Q.10 The Tyndall effect associated with colloidal particles is due to
 (A) presence of electrical charges (B) scattering of light
 (C) absorption of light (D) reflection of light
- Q.11 Which one of the following is not applicable to chemisorption?
 (A) Its heat of adsorption is high (B) It takes place at high temperature
 (C) It is reversible (D) It forms mono-molecular layers
- Q.12 In the colloidal state the particle size ranges
 (A) below 1 nm (B) between 1 nm to 100 nm
 (C) more than 100 nm (D) none of the above
- Q.13 All colloids
 (A) are suspensions of one phase in another
 (B) are two-phase systems
 (C) contain only water-soluble particles
 (D) are true solutions
- Q.14 Colloids can be purified by
 (A) condensation (B) peptization (C) coagulation (D) dialysis

- Q.15 Milk is an example of
 (A) emulsion (B) suspension (C) foam (D) sol.
- Q.16 Colloidal particles in a sol. can be coagulated by
 (A) heating (B) adding an electrolyte
 (C) adding oppositely charged sol (D) any of the above methods
- Q.17 Emulsifier is an agent which
 (A) accelerates the dispersion (B) homogenizes an emulsion
 (C) stabilizes an emulsion (D) aids the flocculation of an emulsion
- Q.18 Fog is a colloidal system of
 (A) gas in liquid (B) liquid in gas (C) gas in gas (D) gas in solid
- Q.19 Given below are a few electrolytes, indicate which one among them will bring about the coagulation of a gold sol. quickest and in the least of concentration?
 (A) NaCl (B) MgSO_4 (C) $\text{Al}_2(\text{SO}_4)_3$ (D) $\text{K}_4[\text{Fe}(\text{CN})_6]$
- Q.20 When a colloidal solution is observed under ultramicroscope, we can see
 (A) light scattered by colloidal particle
 (B) size of the colloidal particle
 (C) shape of the colloidal particle
 (D) relative size of the colloidal particle
- Q.21 Colloidal solutions are classified on the basis of
 (A) molecular size (B) organic or inorganic
 (C) surface tension value (D) pH value
- Q.22 The electrical charge on a colloidal particle is indicated by
 (A) Brownian movement (B) electrophoresis
 (C) ultra microscope (D) molecular sieves
- Q.23 The minimum concentration of an electrolyte required to cause coagulation of a sol is called
 (A) flocculation value (B) gold number (C) protective value (D) none of these
- Q.24 Smoke precipitator works on the principle of
 (A) distribution law (B) neutralization of charge on colloids
 (C) Le-Chatelier's principle (D) addition of electrolytes
- Q.25 Which one of following statements is not correct in respect of lyophilic sols?
 (A) There is a considerable interaction between the dispersed phase and dispersion medium
 (B) These are quite stable and are not easily coagulated
 (C) They carry charge
 (D) The particles are hydrated
- Q.26 As_2S_3 sol is
 (A) positive colloid (B) negative colloid (C) neutral colloid (D) none of the above
- Q.27 Crystalloids differ from colloids mainly in respect of
 (A) electrical behaviour (B) particle nature
 (C) particle size (D) solubility
- Q.28 Which of the following electrolyte will be most effective in coagulation of gold sol.?
 (A) NaNO_3 (B) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (C) Na_3PO_4 (D) MgCl_2
- Q.29 At the critical micelle concentration (CMC) the surfactant molecules
 (A) decompose (B) dissociate
 (C) associate (D) become completely soluble

- Q.30 Alums purify muddy water by
 (A) dialysis (B) absorption (C) coagulation (D) forming true solution
- Q.31 Solute dispersed in ethanol is called
 (A) emulsion (B) micelle (C) hydrophilic sol. (D) alcosols
- Q.32 Which one of the following is lyophilic colloid?
 (A) Milk (B) Gum (C) Fog (D) Blood
- Q.33 Small liquid droplets dispersed in another liquid is called
 (A) suspension (B) emulsion (C) gel (D) true solution
- Q.34 The process which is catalysed by one of the product is called
 (A) acid-base catalysis (B) autocatalysis
 (C) negative catalysis (D) homogeneous catalysis
- Q.35 Tyndall effect would be observed in a
 (A) solution (B) solvent (C) precipitate (D) colloidal sol.
- Q.36 Adsorption is multilayer in case of
 (A) physical adsorption (B) chemisorption
 (C) in both (D) none of these
- Q.37 Crystalloids differ from colloids mainly in respect of
 (A) electrical behaviour (B) particle size
 (C) particle nature (D) solubility
- Q.38 A liquid is found to scatter a beam of light but leaves no residue when passed through the filter paper. The liquid can be described as
 (A) a suspension (B) oil (C) a colloidal sol. (D) a true solution
- Q.39 The ability of an ion to bring about coagulation of a given colloid depends upon
 (A) its charge (B) the sign of the charge alone
 (C) the magnitude of the charge (D) both magnitude and sign of charge
- Q.40 An arsenious sulphide sol. carries a negative charge. The maximum precipitating power of this sol. is possessed by
 (A) K_2SO_4 (B) $CaCl_2$ (C) Na_3PO_4 (D) $AlCl_3$
- Q.41 Reversible adsorption is
 (A) chemical adsorption (B) physical adsorption
 (C) both (D) none
- Q.42 The function of gum arabic in the preparation of Indian ink is
 (A) coagulation (B) peptisation (C) protective action (D) absorption
- Q.43 Which of the following is an example of associated colloid?
 (A) Protein + water (B) Soap + water (C) Rubber + benzene (D) $As_2O_3 + Fe(OH)_3$
- Q.44 Adsorption of gases on solid surface is generally exothermic because
 (A) enthalpy is positive (B) entropy decreases
 (C) entropy increases (D) free energy increases
- Q.45 An emulsifier is a substance
 (A) which stabilises an emulsion
 (B) which breaks the emulsion into its constituent liquids
 (C) which can convert liquid into an emulsion
 (D) which brings about coagulation of an emulsion

Question No. 46 to 50 (5 questions)

Whenever a mixture of gases is allowed to come in contact with a particular adsorbent under the same conditions, the more strong adsorbate is adsorbed to greater extent irrespective of its amount present, e.g. H_2O is adsorbed to more extent on silica gel than N_2 and O_2 . This shows that some adsorbates are preferentially adsorbed. It is also observed that preferentially adsorbable adsorbents can displace a weakly adsorbed substance from the surface of an adsorbent.

- Q.46 Which of the following gases is adsorbed to maximum extent:
 (A) He (B) Ne (C) Ar (D) Xe
- Q.47 Which of the gas can displace remaining all the gases
 (A) O_2 (B) N_2 (C) CO (D) H_2
- Q.48 When temperature is increased
 (A) extent of adsorption increases
 (B) extent of adsorption decreases
 (C) no effect on adsorption
 (D) extent of adsorption first decreases, then increases
- Q.49 Chromatographic separations are based on
 (A) differential solubility (B) differential adsorption
 (C) differential absorption (D) None of these
- Q.50 Activated charcoal is prepared by
 (A) heated charcoal with steam so that it becomes more porous
 (B) adding $\text{Ca}_3(\text{PO}_4)_2$ to charcoal
 (C) adding impurity to charcoal
 (D) reacted with conc. HNO_3

Question No. 51 to 54 (4 questions)

The clouds consist of charged particles of water dispersed in air. Some of them are +vely charged, others are negatively charged. When +vely charged clouds come closer they have cause lightening and thundering whereas when +ve and -ve charged colloids come closer they cause heavy rain by aggregation of minute particles. It is possible to cause artificial rain by throwing electrified sand or silver iodide from an aeroplane and thus coagulation the mist hanging in air.

- Q.51 When excess of AgNO_3 is treated with KI solution, AgI forms
 (A) +ve charged sol (B) -vely charged sol (C) neutral sol (D) true solution
- Q.52 Clouds are colloidol solution of
 (A) liquid in gas (B) gas in liquid (C) liquid in liquid (D) solid in liquid
- Q.53 AgI helps in artificial rain because
 (A) It helps in coagulation (B) It helps in dispersion process
 (C) Both (D) None
- Q.54 Electrical chimneys are made on the principle of
 (A) Electroosmosis (B) Electrophoresis (C) Coagulation (D) All of these

Question No. 55 to 58 (4 questions)

In macromolecular type of colloids, the dispersed particles are themselves large molecules (usually polymers). Since these molecules have dimensions comparable to those of colloidal particles, their dispersions are called macromolecular colloids. Most lyophilic sols belong to this category. There are certain colloids which behave as normal strong electrolytes at low concentrations, but exhibit colloidal properties at higher concentrations due to the formation of aggregated particles. These are known as micelles or associated colloids. Surface active agents like soaps and synthetic detergents belong to this class.

- Critical micelle concentration (CMC) is the lowest concentration at which micelle formation appears. CMC increases with the total surfactant concentration. At concentration higher than CMC, they form extended parallel sheets known as **lamellar micelles** which resemble biological membranes. With two molecules thick, the individual molecule is perpendicular to the sheets such that hydrophilic groups are on the outside in aqueous solution and on the inside is a non-polar medium.
- In concentrated solutions, micelles take the form of long cylinders packed in hexagonal arrays and are called lyotropic mesomorphs.
- In an aqueous solution (polar medium), the polar group points towards the periphery and the hydrophobic hydrocarbon chains point towards the centre forming the core of the micelle.
- Micelles from the ionic surfactants can be formed only above a certain temperature called the **Kraft temperature**.
- They are capable of forming ions
- Molecules of soaps and detergents consist of lyophilic as well as lyophobic parts which associate together to form micelles.
- Micelles may contain as many as 100 molecules or more.

Q.55 Select incorrect statement(s):

- (A) Surface active agent like soaps and synthetic detergents are micelles
 (B) Soaps are emulsifying agents
 (C) $C_{17}H_{35}$ (hydrocarbon part) and $-COO^-$ (carboxylate) part of stearate ion ($C_{17}H_{35}COO^-$) both are hydrophobic
 (D) All are incorrect statements

Q.56 Which part of the soap ($RCOO^-$) dissolves grease and forms micelle?

- (A) R part (called tail of the anion) (B) $-COO^-$ part (called head of the anion)
 (C) both (A) and (B) (D) none of these

Q.57 In multimolecular colloidal sols, atoms or molecules are held together by:

- (A) H-bonding (B) van der Waals forces
 (C) ionic bonding (D) polar covalent bonding

Q.58 Cleansing action of soap occurs because:

- (A) oil and grease can be absorbed into the hydrophobic centres of soap micelles and washed away
 (B) oil and grease can be absorbed into hydrophilic centres of soap micelles and washed away
 (C) oil and grease can be absorbed into both hydrophilic and hydrophobic centres but not washed away
 (D) cleansing action is not related to micelles

Question No.59 to 61 (3 questions)

The protective power of the lyophilic colloids is expressed in terms of gold number a term introduced by Zsigmondy. Gold number is the number of milligram of the protective colloid which prevent the coagulation of 10 ml of red gold sol. when 1 ml of a 10 percent solution of sodium chloride is added to it. Thus, smaller the gold number of lyophilic colloid, the greater is the protective power.

Q.59 On addition of one mL of solution of 10% NaCl to 10 mL of red gold sol in presence of 0.025 g of starch, the coagulation is just prevented. The gold number of starch is

- (A) 0.025 (B) 0.25 (C) 2.5 (D) 25

- Q.60 Which of the following statement(s) is/are correct
 (A) Higher the gold number, more protective power of colloid
 (B) Lower the gold number, more the protective power
 (C) Higher the coagulation value, more the coagulation power
 (D) Lower the coagulation value, higher the coagulation power
- Q.61 Gold number gives an indication of
 (A) protective nature of colloids (B) purity of gold in suspension
 (C) the charge on a colloidal solution of gold (D) g-mole of gold per litre

Question No. 62 & 65 (4 questions)

These questions consist of two statements each, printed as assertion and reason, while answering these questions you are required to choose any one of the following responses.

- (A) If assertion is true but the reason is false.
 (B) If assertion is false but the reason is true.
 (C) If both assertion and reason are true and the reason is a correct explanation of assertion.
 (D) If both assertion and reason are true but reason is not a correct explanation of assertion.

- Q.62 **Assertion :** Isoelectric point is pH at which colloidal can move towards either of electrode
Reason : At isoelectric point, colloidal particles become electrically neutral.
- Q.63 **Assertion :** When AgNO_3 is treated with excess of potassium iodide, colloidal particles gets attracted towards anode.
Reason : Colloidal particles adsorb common ions and thus become charged.
- Q.64 **Assertion :** For adsorption ΔG , ΔH , ΔS all have –ve values
Reason : Adsorption is a spontaneous exothermic process in which randomness decreases due to force of attraction between adsorbent and adsorbate.
- Q.65 **Assertion :** A gas with higher critical temperature gets adsorbed to more extent than a gas with lower critical temperature.
Reason : The easily liquifiable gases get adsorbed to more extent.

Select the correct alternative. (More than one are correct)

- Q.66 Which of the following is/are correct statements
 (A) Hardy Schulz rule is related to coagulation
 (B) Brownian movement and Tyndall effect are shown by colloids
 (C) When liquid is dispersed in liquid, it is called gel.
 (D) Gold number is a measure of protective power of lyophilic colloid.
- Q.67 Which statements is/are correct?
 (A) Physical adsorption is multilayer non-directional and non specific
 (B) Chemical adsorption takes more time to attain equilibrium
 (C) Physical adsorption is due to free valence of atoms
 (D) Chemical adsorption is stronger than physical adsorption
- Q.68 Which of the following is/are correct for lyophilic sols?
 (A) Its surface tension is lower than that of H_2O
 (B) Its viscosity is higher than that of water
 (C) Its surface tension is higher than that of water
 (D) Its viscosity is equal to that of water

- Q.69 Which statement/s is/are correct
 (A) A solution is prepared by addition of excess of AgNO_3 solution in KI solution. The charge likely to develop on colloidal particle is positive.
 (B) The effects of pressure on physical adsorption is high if temperature is low.
 (C) Ultracentrifugation process is used for preparation of lyophobic colloids.
 (D) Gold number is the index for extent of gold plating done.
- Q.70 Colloidal solution can be purified by
 (A) Dialysis (B) Electrodialysis (C) Electrophoresis (D) Ultrafiltration
- Q.71 Coagulation of colloids can be achieved by
 (A) Centrifugation (B) Adding electrolyte (C) Change in pH (D) Adding water
- Q.72 When -vely charged colloid like As_2S_3 sol is added to + vely charged $\text{Fe}(\text{OH})_3$ sol in suitable amounts
 (A) Both the sols are precipitated simultaneously
 (B) This process is called mutual coagulation
 (C) They becomes + vely charged colloid
 (D) They become - vely charged colloid
- Q.73 Which of the following is not lyophillic
 (A) Gelatin sol (B) Silver sol (C) Sulphur sol (D) As_2S_3 sol
- Q.74 Which of the following are multimolecular colloids
 (A) Sulphur sol (B) Egg albumin in water
 (C) Gold sol (D) Soap solution
- Q.75 Colloidal Gold can be prepared by
 (A) Bredig's are method (B) Reduction of AuCl_3
 (C) Hydrolysis (D) Peptization
- Q.76 The coagulation of sol particles may be brought about by
 (A) heating (B) adding oppositely charged sol.
 (C) adding electrolyte (D) persistent dialysis
- Q.77 Which one is not lyophobic in nature?
 (A) Gelatine (B) Sulphur (C) Starch (D) Protein
- Q.78 Which of the following are colloids?
 (A) Milk (B) Ice cream (C) Urea solution (D) Blood
- Q.79 Which are the properties of sols?
 (A) Adsorption (B) Tyndall effect (C) Flocculation (D) Paramagnetism
- Q.80 The migration of colloidal particles under the influence of an electrical field is known as
 (A) electro osmosis (B) electrophoresis (C) electrodialysis (D) None

ANSWER KEY

PROFICIENCY TEST

- Q.1**
- | | | | |
|----------------------|-----------------|---------------------|-------------------------------|
| 1. adsorbent | 2. desorption | 3. electrophoresis | 4. 20–40 kJ·mol ⁻¹ |
| 5. Brownian movement | | 6. more | 7. electrophoresis |
| 8. scattering | 9. emulsions | 10. electro-osmosis | 11. solid in gas |
| 12. adsorption | 13. gold number | 14. emulsion | 15. gel |

Q.2

- | | | | |
|------|-------|------|------|
| 1. T | 2. T | 3. F | 4. F |
| 5. T | 6. T | 7. F | 8. F |
| 9. T | 10. T | | |

Select the correct alternative. (Only one is correct)

- | | | | | | | |
|--------|--------|--------|----------|--------|----------|--------|
| Q.1 B | Q.2 D | Q.3 C | Q.4 B | Q.5 D | Q.6 A | Q.7 B |
| Q.8 B | Q.9 C | Q.10 B | Q.11 C | Q.12 B | Q.13 B | Q.14 D |
| Q.15 A | Q.16 D | Q.17 C | Q.18 B | Q.19 C | Q.20 A | Q.21 A |
| Q.22 B | Q.23 A | Q.24 B | Q.25 C | Q.26 B | Q.27 C | Q.28 D |
| Q.29 C | Q.30 C | Q.31 D | Q.32 B | Q.33 B | Q.34 B | Q.35 D |
| Q.36 A | Q.37 C | Q.38 D | Q.39 D | Q.40 D | Q.41 B | Q.42 C |
| Q.43 B | Q.44 B | Q.45 A | Q.46 D | Q.47 C | Q.48 B | Q.49 B |
| Q.50 A | Q.51 A | Q.52 A | Q.53 C | Q.54 B | Q.55 C,D | Q.56 C |
| Q.57 B | Q.58 A | Q.59 D | Q.60 B,D | Q.61 A | Q.62 B | Q.63 D |
| Q.64 C | Q.65 C | | | | | |

Select the correct alternative. (More than one are correct)

- | | | | |
|------------|------------|----------|------------|
| Q.66 A,C,D | Q.67 B | Q.68 A,B | Q.69 A,B |
| Q.70 A,B,D | Q.71 A,B,C | Q.72 A,B | Q.73 B,C,D |
| Q.74 A,C | Q.75 A,B | Q.76 B,C | Q.77 B,C |
| Q.78 A,B,D | Q.79 A,B,C | Q.80 B | |

STUDY PACKAGE

Target: IIT-JEE (Advanced)

SUBJECT: CHEMISTRY-XII

TOPIC: 9. Chemical Kinetics

Index:

- 1. Key Concepts**
- 2. Exercise I**
- 3. Exercise II**
- 4. Exercise III**
- 5. Exercise IV**
- 6. Answer Key**
- 7. 34 Yrs. Que. from IIT-JEE**
- 8. 10 Yrs. Que. from AIEEE**

THE KEY

CHEMICAL KINETICS :

It is a branch of physical chemistry deals with the "Rate of Chemical Reactions" including the effect of temperature, pressure, concentration, etc., on the rates, and the mechanism by which the reaction takes place.

RATE OF CHEMICAL REACTION is defined as the change in concentration of a reactant (or a product) in a particular time interval. Average rate of reaction, Instantaneous rate of reaction.

Units of Reaction Rate are unit of concentration divided by the unit of time ($\text{mol L}^{-1}\text{s}^{-1}$ or $\text{mol L}^{-1}\text{min}^{-1}$ or so on).

FACTORS AFFECTING REACTION RATES :

- (i) Concentration of reactants and
- (ii) Reaction temperature

Besides these, presence of catalyst and surface area (if a reactant or a catalyst is a solid) exposure to radiation also affect the reaction rates.

EXPRESSIONS OR THE RATE :

For a general reaction : $aA + bB \longrightarrow cC + dD$,

The rate of disappearance of A = $-\frac{d[A]}{dt}$; Rate of disappearance of B = $-\frac{d[B]}{dt}$;

Rate of appearance of C = $\frac{d[C]}{dt}$ & Rate of appearance of D = $\frac{d[D]}{dt}$.

The positive sign shows that concentrations of C and D increases with time and the negative sign indicating that concentrations of A and B decrease with time. Thus the rate of general reaction.

$$\text{rate : } -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} .$$

RATE EQUATION AND RATE CONSTANT :

An expression which relates the rate of a reaction to the concentration of the reactants is called the *Rate Equation or Rate Law*. $\text{Rate} \propto [A]^a \cdot [B]^b$ or $\text{Rate} = k [A]^a [B]^b$. The constant of proportionality, k is known as the *Rate Constant* (specific reaction rate) and may be defined as the rate at unit concentrations of the reactants. k depends on the temperature and is independent of the initial concentrations of the reactants. At a fixed temperature, k is constant characteristic of the reaction. Larger value of k indicates fast reaction and small k indicates slow reactions.

MOLECULARITY :

Molecularity of a reaction is defined as the numbers of particles (atoms, ions, groups or molecules) of reactants actually taking part in a single step chemical reaction.

Molecularity of a reaction is :

- (i) Always a whole number (not zero) and never a fraction.
- (ii) The value of molecularity of a simple or one step reaction does not exceed 3.

ORDER OF REACTION :

It is defined as the sum of the exponents (powers) of the molar concentrations of the reactants in the experimentally determined rate equations.

If rate of reaction $\propto [A]^p [B]^q [C]^r$ or Rate of reaction = $k [A]^p [B]^q [C]^r$

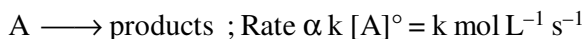
order of reaction = $p + q + r$ & the order w.r.t. A, B & C are p, q & r respectively.

For a "Reaction of n^{th} order", the order of the reaction is n and the rate equation (or Rate law) is $\text{rate} \propto [A]^n = k [A]^n$.

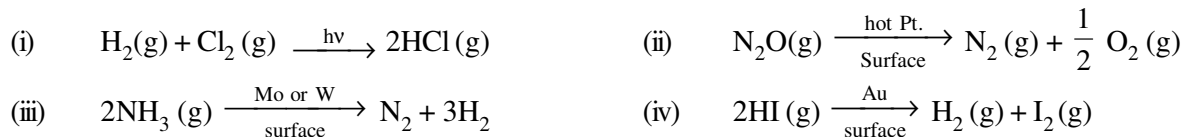
The order of a reaction is obtained from the experimentally determined rate (and not from the stoichiometric equation) and may be zero, an integer or a fraction and never exceeds 3. In a multi-step complex reaction, the order of the reaction depends on the slowest step.

ZERO ORDER REACTION :

A reaction is said to be of zero order if the rate is independent of the concentration of the reactants.



EXAMPLES :

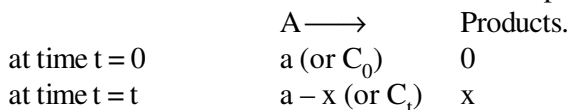


CHARACTERISTICS OF ZERO ORDER REACTION :

- (1) Concentration of reactant decreases linearly with time. $[A]_t = [A]_0 - kt$.
- (2) Units of k are, $\text{mol l}^{-1} \text{ time}^{-1}$.
- (3) Time required for the completion of reaction $t = \frac{[A]_0}{k}$ & $t_{1/2} = \frac{0.5 [A]_0}{k}$

FIRST ORDER REACTION :

A reaction is said to be of first order if its rate is proportional to the concentration of one reactant only.



$$\text{Rate} \propto [A] = k_1 [A] \text{ or } \frac{dx}{dt} = k_1(a - x) \quad (1 \text{ st order differential equation})$$

$$\text{Integrated 1 st order rate equation is } k_1 = \frac{2.303}{t} \log \frac{a}{a - x}.$$

$$\text{Exponential form of 1 st order equation is } C_t = C_0 e^{-k_1 t}$$

Characteristics Of First Order Reaction :

- (1) Unit of rate constant is time^{-1} .
- (2) Change in concentration unit will not change the numerical value of k_1 .
- (3) $t_{1/2} = \frac{0.693}{k_1}$ (Half-life); Average life $= \frac{1}{k}$;
- (4) $\log(a - x)$ v/s t is a straight line with slope $-\frac{k_1}{2.303}$.

EXAMPLES :

- (i) Radioactive disintegration is a first order reaction.
- (ii) $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow[\text{Inversion}]{\text{H}^+ \text{ catalysed hydrolysis}} \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$
(glucose) (fructose)
- (iii) Mineral acid catalyzed hydrolysis of esters.
- (iv) Decomposition of H_2O_2 in aqueous solution.

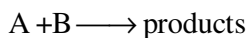
SECOND ORDER REACTION :

- (i) When two molecules of the same reactant are involved or the concentrations of the both reactants are equal reactions $2A \longrightarrow \text{products}$ or $A + B \longrightarrow \text{products}$.

$$\text{Differential rate equation } \frac{dx}{dt} = k_2(a - x)^2$$

$$\text{Integrated rate equation } k_2 = \frac{1}{t} \cdot \frac{x}{a(a - x)} \text{ or } k_2 t = \frac{1}{a - x} - \frac{1}{a}.$$

- (ii) When the initial concentrations of the two reactants are different;



a b

differential rate equation $\frac{dx}{dt} = k_2 (a - x)(b - x)$.

$$\text{Integrated rate equation } k_2 = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$$

CHARACTERISTICS OF SECOND ORDER REACTION :

- (i) Unit of rate constant $L \text{ mol}^{-1} \text{ time}^{-1}$.
- (ii) Numerical value of k will depend upon unit of concentration.
- (iii) $t_{1/2} \propto a^{-1}$ (In general $t_{1/2} \propto a^{(1-n)}$; n = order of reactions).
- (iv) 2nd order reaction conforms to first order when one of the reactant in excess.

EXAMPLES :

- (i) Saponification (hydrolysis of esters catalysed with alkali).
 $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$
- (ii) Hydrogenation of ethane $\text{C}_2\text{H}_4 + \text{H}_2 \xrightarrow{100^\circ\text{C}} \text{C}_2\text{H}_6$.
- (iii) $2 \text{O}_3 \longrightarrow 3 \text{O}_2$.

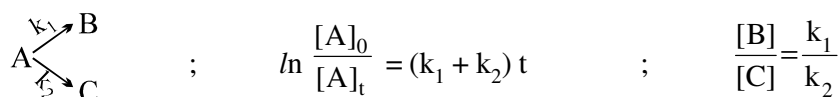
n^{th} ORDER REACTION.



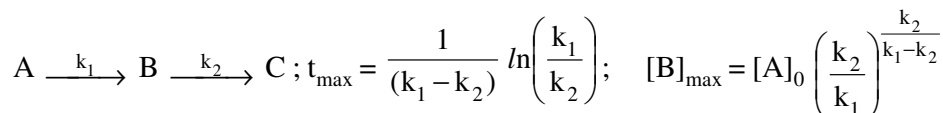
$$k_n t = \frac{1}{n-1} \left\{ \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right\} \quad [n \neq 1, n = \text{order}]$$

$$t_{1/2} = \frac{1}{k_n(n-1)} \cdot \left[\frac{2^{n-1} - 1}{a^{n-1}} \right]$$

SIDE OR CONCURRENT REACTION :



CONSECUTIVE REACTION :



THRESHOLD ENERGY AND ACTIVATION ENERGY :

For a reaction to take place the reacting molecules must collide together, but only those collisions, in which colliding molecules possess certain minimum energy is called threshold energy (E_T).

ACTIVATION ENERGY (E_a) :

The extra energy needed for the reactant molecules to be able to react chemically is known as Activation energy.

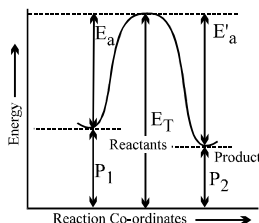
E_T = Threshold energy

E_a = Activation energy of forward reaction

E'_a = activation energy of backward reaction

P_1 = Potential energy of reactants

P_2 = Potential energy of products



INFLUENCE OF TEMPERATURE ON REACTION RATES :

TEMPERATURE COEFFICIENT :

The temperature coefficient of a chemical reaction is defined as the ratio of the reaction rates at two temperatures differing by 10°C. Its value usually lies between 2 & 3.

$$\text{Temperature coefficient} = \frac{k_{t+10}}{k_t}.$$

ARRHENIUS EQUATION :

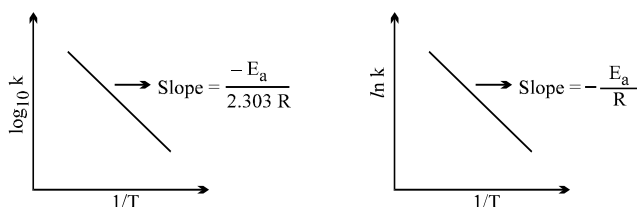
A quantitative relationship was proposed by Arrhenius $k = A \cdot e^{-E_a/RT}$ Where,

k = rate constant ; A = frequency factor (or pre – exponential factor);

R = gas constant ; T = Temperature (kelvin) ; E_a = Activation energy.

The Logarithmic expressions are $\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$; Vant Hoff's Isochore $\frac{d}{dt} \ln k = \frac{E_a}{RT^2}$

GRAPHICAL REPRESENTATIONS ARE :



METHODS OF DETERMINATION OF ORDER OF REACTIONS :

A few methods commonly used are given below :

1. **Hit & Trial Method** : It is method of using integrated rate equations, where the experimental values of a , x & t are put into these equations. One which gives a constant value of k for different sets of a , x & t correspond to the order of the reaction.
2. **Graphical Method** :
 - (i) A plot of $\log(a - x)$ versus ' t ' gives a straight lines for the First order reaction.
 - (ii) A plot of $(a - x)^{-(n-1)}$ versus ' t ' gives a straight line any reaction of the order n (except $n = 1$).

3. **Half Life Method** : The half life of different order of reactions is given by $a_n = \left(\frac{1}{2}\right)^n a_0$.

By experimental observation of the dependence of half life on initial concentration we can determine n ,

$$\text{the order of reaction. } n = 1 + \frac{\log t_2 - \log t_1}{\log a_1 - \log a_2}.$$

4. **Initial rate method.** Initial rate method is used to determine the order or reaction in cases where more than one reactant is used. It involves the determination of the order of different reactants separately. A series of experiments are performed in which concentration of one particular reactant is varied whereas conc. of other reactants are kept constant. In each experiment the initial rate is determined from the plot of conc. vs. time, e.g., if conc. of A is doubled, and initial rate of reaction is also doubled, order of reaction is 1.

MECHANISM OF REACTIONS :

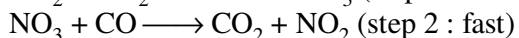
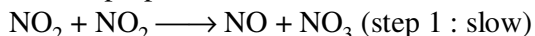
The path way which reactants are converted into the products is called the reaction mechanism. It should be clear that experimentally determined rate expression cannot be predicted from the stiochiometry of the reaction. For example for the reaction ;

$\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + \text{NO}(\text{g})$, the rate expression is ; $\text{rate} = -\frac{d}{dt} [\text{NO}_2] = k[\text{NO}_2]^2$,
i.e. the expression has no dependence of $\text{CO}(\text{g})$ concentration.

The reason is that the reaction occurs by a series of elementary steps.

The sequence of elementary processes leading to the overall stoichiometry is known as the "Mechanism of the reaction". A_n in a sequence of reactions leading to the formation of products from reactants, the slowest step is the rate determining step.

The mechanism proposed for the above reaction is a two step one.

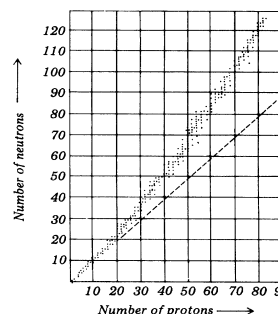


The sum of the two gives the stoichiometry & the slow step decided the rate expression.

Nuclear Chemistry

Neutron / proton ratio and stability

- ▶▶ For atomic number < 20, most stable nuclei have n: p ratio nearly 1 : 1 (except H & Ar).
- ▶▶ For n/p ratio > 1.5, nucleus is unstable. Largest stable nucleus is $^{209}_{83}\text{Bi}$ for which n/p ratio is 1.52.
- ▶▶ For atomic number > 83, there are no stable nuclei.



Magic numbers and nuclear stability

Nuclei with 2, 8, 20, 28, 50, 82 or 126 protons or neutrons are unusually stable and have a larger number of stable isotopes than neighboring nuclei in the periodic table. These numbers are called magic numbers. They are supposed to represent completely filled nuclear shells of energy levels.

- ▶▶ Nuclei with magic number of protons as well as neutrons have notably high stabilities. [eg. ^4_2He , $^{16}_8\text{O}$, $^{40}_{20}\text{Ca}$ and $^{208}_{82}\text{Pb}$]. 165 such stable nuclei are known.
- ▶▶ There exist 55 known nuclei with even number of protons and odd number of neutrons, and 50 known stable nuclei with odd number of protons and even number of neutrons. On the other hand, the number of known stable nuclei having odd numbers of both neutrons and protons is only 4.

Expected emissions from unstable nucleus

1. **n/p ratio above stability belt:** electron (β^-) or neutron.
2. **n/p ratio below stability belt:** positron (β^+) or K capture.
3. **Atomic number > 83,** various particles, including α -particles.

Radioactive decay

- ▶▶ Radioactive decay is a first order process. Hence $-\frac{dN}{dt} = \lambda N$ or $N = N_0 e^{-\lambda t}$

where N = number of radioactive nuclei at any time t ; N_0 = number of radioactive nuclei at $t = 0$; λ = decay constant.

- ▶▶ **Activity** activity (a) = $-\frac{dN}{dt} = \lambda N$

S.I. units : disintegration per second (symbol s^{-1} or dps). This unit is also called *becquerel* (symbol Bq)

Other units: Curie (Ci) $1\text{Ci} = 3.7 \times 10^{10}\text{dps}$.

- ▶▶ **Half life ($t_{1/2}$)** The time taken by half the nuclei (originally present) to decay. $t_{1/2} = 0.693/\lambda$
Note : After n half-lives have passed, activity is reduced to $\frac{1}{2^n}$ of its initial value.

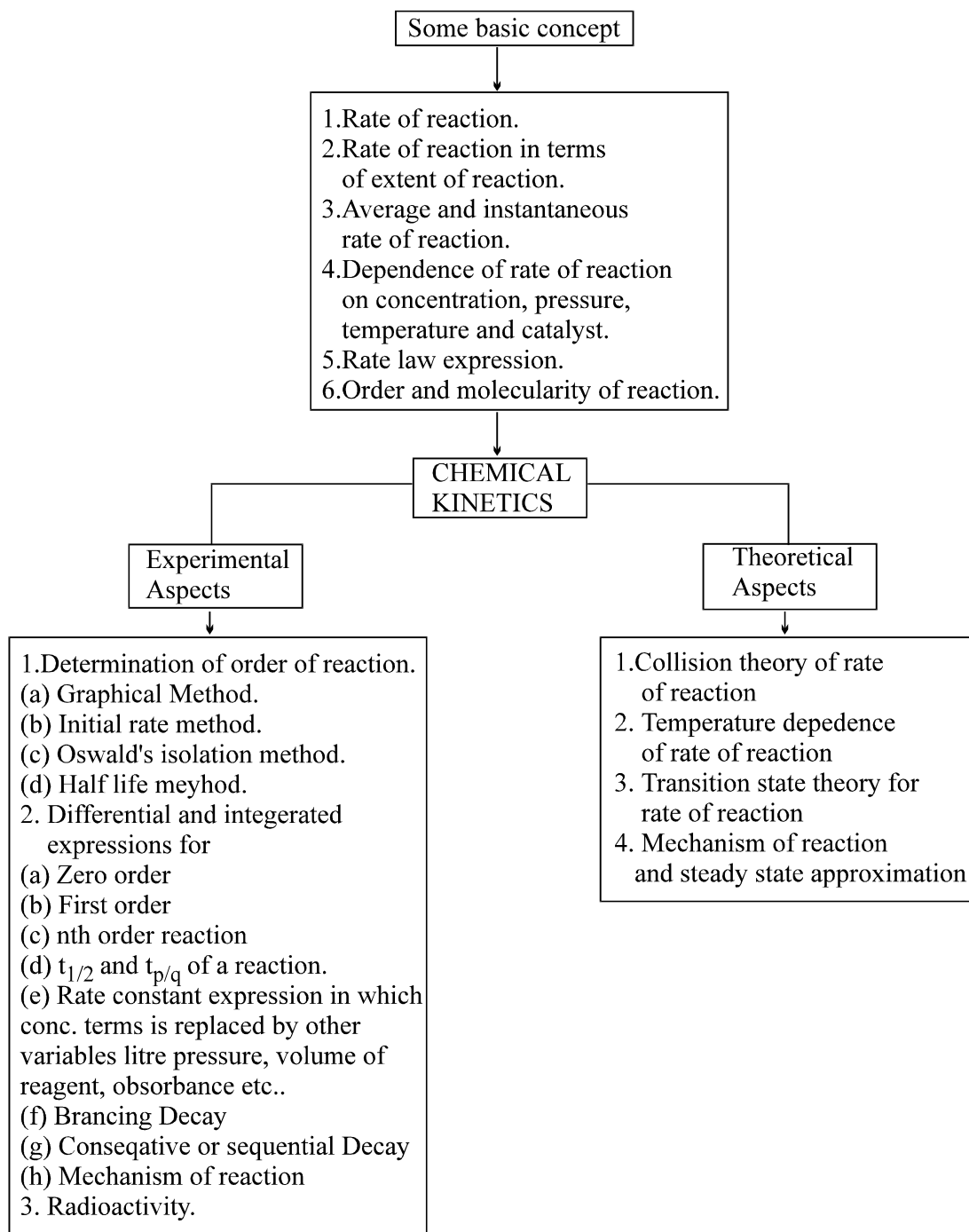
- ▶▶ **Average life (t_{av})** $t_{av} = 1/\lambda = 1.44 t_{1/2}$

Isotopes : Nuclei with same atomic number but different atomic mass number.

Isobars : Nuclei with different atomic number but same atomic mass number.

Isotones : Nuclei with same number of neutrons but different number of protons.

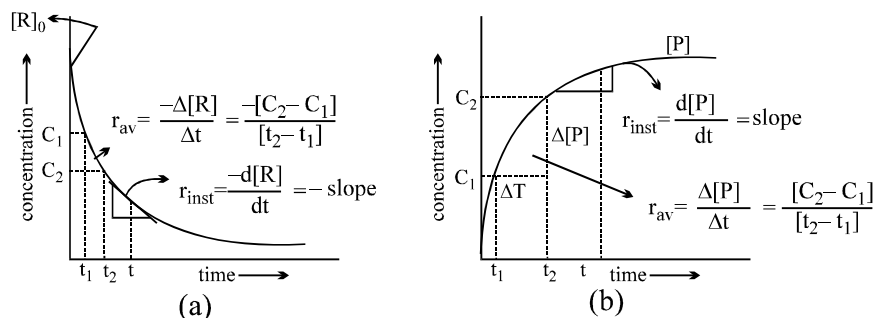
THE ATLAS



GLOSSARY

IMPORTANT TERMS AND DEFINITIONS

1. **Rate of reaction.** It is defined as the change in concentration of reactant (or product) in a particular time interval. Its unit is $\text{mol L}^{-1}\text{s}^{-1}$. If time is in minutes, then units are $\text{mol L}^{-1}\text{min}^{-1}$ and so on.
2. **Average rate.** The rate of reaction measured over a long time interval is called average rate of reaction. It is equal to $\Delta x/\Delta t$ as shown in fig.(a) and (b).



Instantaneous and average rate of reaction

3. **Instantaneous rate.** It is the rate of reaction when the average rate is taken over a very small interval of time. It is equal to dx/dt as shown in fig. (a) and (b).
4. **Rate law or rate equation.** It is the expression which relates the rate of reaction with concentration of the reactants. The constant of proportionality 'k' is known as rate constant.
5. **Rate constant.** When concentration of both reactants are unity, then the rate of reaction is known as rate constant. It is also called specific reaction rate.
6. **Molecularity.** Total number of molecules of the reactants involved in the reaction is termed as its molecularity. It is always in whole number, It is never more than three. It cannot be zero.
7. **Order of a reaction.** The sum of the powers of the concentration of reactants in the rate law is termed as order of the reaction. It can be in fraction. It can be zero also.
8. **Zero order reaction.** The rate of reaction does not change with the concentration of the reactants, i.e.,

$$\text{rate} = k[A]^0$$
9. **First order reaction.** The reaction in which the rate of reaction is directly proportional to the concentration of reacting substance. Rate constant of first order reaction is

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{or} \quad k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

where 'a' is initial concentration, (a-x) is the conc. of reactants after time 't'. The unit of 'k' is s^{-1} or min^{-1} . A plot between $\ln [A]$ vs. t is a straight line with slope equal to $-k$. [A] is concentration of reactants after time t .

10. **Half-life of a reaction.** The time taken for a reaction when half of the starting material has reacted is called half-life of a reaction. For first order reaction

$$t_{1/2} = \frac{0.693}{k}, \text{ where } k \text{ is rate constant.}$$

11. **Second order reaction.** The reaction in which sum of powers of concentration terms in rate law or rate equation is equal to 2, e.g.,

$$\frac{dx}{dt} = k[A]^1[B]^1$$

12. **Third order reaction.** The reaction in which sum of powers of concentration terms in rate law or rate equation is equal to 3, e.g.,

$$\frac{dx}{dt} = k[A]^x[B]^y \text{ where } x + y = 3$$

13. **Specific rate constant (k).** It is defined as equal to rate of reaction when molar concentration of reactant is unity.
14. **Activation energy.** It is extra energy which must be possessed by reactant molecules so that collision between reactant molecules is effective and leads to formation of product molecules.
15. **Initial rate.** The rate at the beginning of the reaction when the concentrations have not changed appreciably is called in initial rate of reaction.
16. **Arrhenius equation of reaction rate.** It gives the relation between rate of reaction and temperature.

$$K = Ae^{-E_a/RT}$$

where k = rate constant A = frequency factor, E_a = energy of activation

R = gas constant, T = temperature in kelvin.

$$\ln k = \ln A - E_a/RT$$

$$\log k = \log A - \frac{E_a}{2.303 RT}$$

17. **Photochemical reactions.** Those reactions which take place in the presence of light are called photochemical reactions. Photosynthesis is an example of photochemical reaction.
18. **Photosensitization.** The process in which a molecule that absorbs light transfers its extra energy to another molecule which may undergo a reaction. This process is called photosensitization.
19. **Chain reaction.** The sequence of reactions, where a reactive species produces more reactive species is called chain reaction. It involves free radicals.
20. **Elementary processes.** Some reactions occur by a series of elementary steps and such simple steps are called elementary processes.
21. **Mechanism of reaction.** The sequence of elementary processes leading to the overall stoichiometry of a chemical reaction is known as mechanism of a reaction.
22. **Slow reaction.** Those reactions which take place very slowly are called slow reactions, e.g., rusting of iron and reaction of oxalic acid with acidified KMnO_4 at room temperature are slow reactions.
23. **Life time.** The time in which 98% of the reaction is complete is called lifetime.
24. **Threshold energy.** The minimum energy that reacting species must possess in order to undergo effective collision to form product molecules is called threshold energy.
25. **Effective collision (f).** Those collisions which lead to the formation of product molecules are called effective collisions. Rate of reaction = $f \times z$ where 'z' is collision frequency and 'f' is fraction of collisions, which are effective.
26. **Collision frequency (z).** It is defined as total number of collisions per unit volume per unit time.
27. **Activated complex.** It is defined as unstable intermediate formed between reacting molecules which is highly unstable and readily changes into product.
28. **Thermodynamic stability.** A mixture of substances may not undergo reaction although thermodynamic predict the reaction to be spontaneous. Such substances are thermodynamically unstable at ordinary temperature but may not be kinetically unstable.
29. **Kinetic stability.** The reaction occurs only when the reactant crosses energy-barrier. Once it occurs, it becomes kinetically unstable because the reaction is spontaneous. The energy evolved helps the other reactants to cross energy-barrier. Thus, reactants should be thermodynamically as well as kinetically unstable so as to change into products at a particular temperature.

30. **Rate determining step.** The slowest step in the reaction mechanism is called rate determining step.
31. **Temperature coefficient.** It is the ratio of rate constant at temperature 308 K to the rate constant at temperature 298 K.
- $$\text{Temperature coefficient} = \frac{\text{Rate constant 'k' at } 308 \text{ K}}{\text{Rate constant 'k' at } 298 \text{ K}}$$
- It lies between 2 and 3.
32. **Pseudo first order reaction.** The reaction in which one reactant is in excess so order is one is called Pseudo first order reaction, e.g., acidic hydrolysis of ester.
- $$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O (excess)} \xrightleftharpoons{\text{H}^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$$
33. **Einstein's law of photochemical equivalence.** Each atom or molecule is activated by 1 photon (quantum of light).
34. **Chain initiation step.** The step in which neutral molecule changes into free radicals by absorbing photons is called chain initiation step.
35. **Chain propagation step.** The step in which free radical reacts with neutral molecule to form a neutral molecule and a free radical is called chain propagation step.
36. **Chain termination step.** The step in which radicals combine to form neutral molecules.
37. **Fast reactions.** Those reactions which occur instantaneously and are complete in fraction of seconds are called fast reactions, e.g., $\text{AgNO}_3(\text{aq}) + \text{HCl}(\text{aq}) \longrightarrow \text{AgCl} \downarrow + \text{HNO}_3$, takes place in 10^{-12} seconds.
38. **Thermochemical reactions.** Those reactions initiated by heat energy are called thermochemical reactions. They can occur in dark. Temperature coefficient is generally high because rate of reaction increases with increase in temperature. ΔG is – ve for such reactions.

EXERCISE-I
RATE OF REACTION AND STOICHIOMETRIC COEFFICIENT

- Q.1 In a catalytic experiment involving the Haber process, $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$, the rate of reaction was measured as

$$\text{Rate} = \frac{\Delta[\text{NH}_3]}{\Delta t} = 2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}.$$

If there were no side reactions, what was the rate of reaction expressed in terms of (a) N_2 , (b) H_2 ?

- Q.2 For the reaction $3\text{BrO}^- \longrightarrow \text{BrO}_3^- + 2\text{Br}^-$ in an alkaline aqueous solution, the value of the second order (in BrO^-) rate constant at 80°C in the rate law for $-\frac{\Delta[\text{BrO}^-]}{\Delta t}$ was found to be $0.056 \text{ L mol}^{-1} \text{ s}^{-1}$.

What is the rate of constant when the rate law is written for (a) $\frac{\Delta[\text{BrO}_3^-]}{\Delta t}$, (b) $\frac{\Delta[\text{Br}^-]}{\Delta t}$?

- Q.3 Dinitropentaoxide decomposes as follows :



Given that $-\text{d}[\text{N}_2\text{O}_5] / \text{dt} = k_1[\text{N}_2\text{O}_5]$

$$\text{d}[\text{NO}_2] / \text{dt} = k_2[\text{N}_2\text{O}_5]$$

$$\text{d}[\text{O}_2] / \text{dt} = k_3[\text{N}_2\text{O}_5]$$

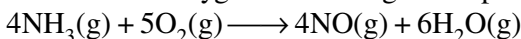
What is the relation between k_1 , k_2 and k_3 ?

- Q.4 The reaction $2\text{A} + \text{B} + \text{C} \longrightarrow \text{D} + \text{E}$ is found to be 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 concentrations of A, B, and C two times?

- Q.5 For the elementary reaction $2\text{A} + \text{B}_2 \longrightarrow 2\text{AB}$. Calculate how much the rate of reaction will change if the volume of the vessel is reduced to one third of its original volume?

- Q.6 Ammonia and oxygen reacts at higher temperatures as



In an experiment, the concentration of NO increases by $1.08 \times 10^{-2} \text{ mol litre}^{-1}$ in 3 seconds. Calculate.

- (i) rate of reaction.
- (ii) rate of disappearance of ammonia
- (iii) rate of formation of water

- Q.7 In the following reaction $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$
rate of formation of O_2 is 3.6 M min^{-1} .

- (a) What is rate of formation of H_2O ?
- (b) What is rate of disappearance of H_2O_2 ?

- Q.8 The reaction $\text{A}(\text{g}) + 2\text{B}(\text{g}) \longrightarrow \text{C}(\text{g}) + \text{D}(\text{g})$ is an elementary process. In an experiment, the initial partial pressure of A & B are $P_A = 0.6$ and $P_B = 0.8 \text{ atm}$, if $P_C = 0.2 \text{ atm}$ then calculate the ratio of rate of reaction relative to initial rate.

ZERO ORDER

- Q.9 In the following reaction, rate constant is $1.2 \times 10^{-2} \text{ M s}^{-1}$ $\text{A} \longrightarrow \text{B}$. What is concentration of B after 10 and 20 min., if we start with 10 M of A.

- Q.10 For the following data for the reaction $\text{A} \longrightarrow \text{products}$. Calculate the value of k.

Time (min.)	[A]
0.0	0.10 M
1.0	0.09 M
2.0	0.08 M

- Q.11 The rate constant for a zero order reaction is $2 \times 10^{-2} \text{ mol L}^{-1} \text{ sec}^{-1}$, if the concentration of the reactant after 25 sec is 0.25 M, calculate the initial concentration.
- Q.12 A drop of solution (volume 0.10 ml) contains 6×10^{-6} mole of H^+ , if the rate constant of disappearance of H^+ is $1 \times 10^7 \text{ mole litre}^{-1} \text{ sec}^{-1}$. How long would it take for H^+ in drop to disappear?
- Q.13 A certain substance A is mixed with an equimolar quantity of substance B. At the end of an hour A is 75% reacted. Calculate the time when A is 10% unreacted. (Given: order of reaction is zero)

FIRST ORDER

- Q.14 A first order reaction is 75% completed in 72 min.. How long time will it take for
(i) 50% completion (ii) 87.5% completion
- Q.15 A first order reaction is 20% complete in 10 min. calculate (i) the specific rate constant, (ii) the time taken for the reactions to go to 75% completion.
- Q.16 Show that in case of unimolecular reaction, the time required for 99.9% of the reaction to take place in ten times that required for half of the reaction.
- Q.17 A first order reaction has a rate constant is $1.5 \times 10^{-3} \text{ sec}^{-1}$. How long will 5.0 g of this reactant take to reduce to 1.25 g.
- Q.18 A drug is known to be ineffective after it has decomposed 30%. The original concentration of a sample was 500 units/ml. When analyzed 20 months later, the concentration was found to be 420 units/ml. Assuming that decomposition is of I order, what will be the expiry time of the drug?
- Q.19 A viral preparation was inactivated in a chemical bath. The inactivation process was found to be first order in virus concentration. At the beginning of the experiment 2.0 % of the virus was found to be inactivated per minute. Evaluate k for inactivation process.
- Q.20 If a reaction $\text{A} \longrightarrow \text{Products}$, the concentrations of reactant A are $C_0, aC_0, a^2C_0, a^3C_0, \dots$ after time interval 0, t, 2t, 3t, where a is a constant. Given $0 < a < 1$. Show that the reaction is of first order. Also calculate the relation in k, a and t.
- Q.21 The reaction $\text{SO}_2\text{Cl}_2(\text{g}) \longrightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ is a first order gas reaction with $k = 2.2 \times 10^{-5} \text{ sec}^{-1}$ at 320°C . What % of SO_2Cl_2 is decomposed on heating this gas for 90 min.

ORDER OF REACTION & RATE LAW

- Q.22 At 800°C the rate of reaction
 $2 \text{ NO} + \text{H}_2 \longrightarrow \text{N}_2 + \text{H}_2\text{O}$
 Changes with the concentration of NO and H_2 are

	[NO] in M	[H ₂] in M	$-\frac{1}{2} \frac{d[\text{NO}]}{dt}$ in M sec ⁻¹
(i)	1.5×10^{-4}	4×10^{-3}	4.4×10^{-4}
(ii)	1.5×10^{-4}	2×10^{-3}	2.2×10^{-4}
(iii)	3.0×10^{-4}	2×10^{-3}	8.8×10^{-4}

- (a) What is the order of this reaction?
 (b) What is the rate equation for the reaction?
 (c) What is the rate when
 $[\text{H}_2] = 1.5 \times 10^{-3} \text{ M}$ and $[\text{NO}] = 1.1 \times 10^{-3} \text{ M}$?

Q.23 The data below are for the reaction if NO and Cl₂ to form NOCl at 295 K

Concentration of Cl ₂ [M]	Concentration of NO	Initial Rate (M s ⁻¹)
0.05	0.05	1 × 10 ⁻³
0.15	0.05	3 × 10 ⁻³
0.05	0.15	9 × 10 ⁻³

- What is the order w.r.t NO and Cl₂ in the reaction.
- Write the rate expression
- Calculate the rate constant
- Determine the reaction rate when concentration of Cl₂ and NO are 0.2 M & 0.4 M respectively.

Q.24 The catalytic decomposition of N₂O by gold at 900°C and at an initial pressure of 200mm is 50% complete in 53 minutes and 73% complete in 100 minutes.

- What is the order of the reaction?
- Calculate the velocity constant.
- How much of N₂O will decompose in 100 min. at the same temperature but at initial pressure of 600 mm?

Q.25 The following data are for the reaction A + B → products:

Conc. A (M)	Conc. B (M)	Initial Rate (mol L ⁻¹ s ⁻¹)
0.1	0.1	4.0 × 10 ⁻⁴
0.2	0.2	1.6 × 10 ⁻³
0.5	0.1	2.0 × 10 ⁻³
0.5	0.5	1.0 × 10 ⁻²

- What is the order with respect to A and B for the reaction?
- Calculate the rate constant.
- Determine the reaction rate when the concentrations of A and B are 0.2M and 0.35M, respectively.

Q.26 The pressure of a gas decomposing at the surface of a solid catalyst has been measured at different times and the results are given below

t (sec)	0	100	200	300
Pr. (Pascal)	4 × 10 ³	3.5 × 10 ³	3 × 10 ³	2.5 × 10 ³

Determine the order of reaction, its rate constant.

Q.27 The half life period of decomposition of a compound is 50 minutes. If the initial concentration is halved, the half life period is reduced to 25 minutes. What is the order of reaction?

Q.28 At 600°C, acetone (CH₃COCH₃) decomposes to ketene (CH₂ = C = O) and various hydrocarbons. Given the initial rate data in the table:

- What is the order?
 - Write rate law
 - Calculate rate constant
 - Calculate the rate of decomposition when the acetone concentration is 1.8 × 10⁻³ M
- | Experiment | Initial [CH ₃ COCH ₃] | Rate M s ⁻¹ |
|------------|--|------------------------|
| 1. | 6.0 × 10 ⁻³ M | 5.2 × 10 ⁻⁵ |
| 2. | 9.0 × 10 ⁻³ M | 7.8 × 10 ⁻⁵ |
| 3. | 1.8 × 10 ⁻³ M | ? |

HALF LIFE

Q.29 The half life period of a first order reaction is 50 min. In what time will it go to 90% completion?

Q.30 A first order reaction has k = 1.5 × 10⁻⁶ per second at 200°C. If the reaction is allowed to run for 10 hrs., what percentage of the initial concentration would have changed into the product? What is the half life of this reaction?

- Q.31 Show that in case of a first order reaction, the time required for 93.75% of the reaction to take place is four times that required for half of the reaction.
- Q.32 The half time of the first order decomposition of nitramide is 2.1 hour at 15°C.

$$\text{NH}_2\text{NO}_2 (\text{aq.}) \longrightarrow \text{N}_2\text{O} (\text{g}) + \text{H}_2\text{O} (\text{l})$$
 If 6.2 g of NH_2NO_2 is allowed to decompose, calculate (i) time taken for NH_2NO_2 to decompose 99%, and (ii) volume of dry N_2O produced at this point, measured at STP.
- Q.33 A flask contains a mixture of compounds A and B. Both compounds decompose by first-order kinetics. The half-lives are 54.0 min for A and 18.0 min. for B. If the concentrations of A and B are equal initially, how long will it take for the concentration of A to be four times that of B?
- Q.34 Two substances A ($t_{1/2} = 5$ mins) and B ($t_{1/2} = 15$ mins) follow first order kinetics are taken in such a way that initially $[A] = 4[B]$. Calculate the time after which the concentration of both the substance will be equal.

CONCENTRATION REPLACED BY OTHER QUANTITIES IN FIRST ORDER
INTEGRATED RATE LAW

- Q.35 In this case we have

$$\text{A} \longrightarrow \text{B} + \text{C}$$

Time	t	∞
Total pressure of A + B + C	P_2	P_3

 Find k.
- Q.36
$$\text{A} \longrightarrow \text{B} + \text{C}$$

Time	t	∞
Total pressure of (B + C)	P_2	P_3

 Find k.
- Q.37
$$\text{A} \longrightarrow \text{B} + \text{C}$$

Time	0	t
Volume of reagent	V_1	V_2

 The reagent reacts with A, B and C. Find k.
- Q.38
$$\text{A} \longrightarrow 2\text{B} + 3\text{C}$$

Time	t	∞
Volume of reagent	V_2	V_3

 Reagent reacts with all A, B and C. Find k.
- Q.39
$$\text{S} \longrightarrow \text{G} + \text{F}$$

Time	t	∞
Rotation of Glucose & Fructose	r_t	r_∞

 Find k.
- Q.40 At 27°C it was observed during a reaction of hydrogenation that the pressure of hydrogen gas decreases from 2 atmosphere to 1.1 atmosphere in 75 minutes. Calculate the rate of reaction (in M sec^{-1}) and rate of reaction in terms of pressure.
- Q.41 At 100°C the gaseous reaction $\text{A} \longrightarrow 2\text{B} + \text{C}$ was observed to be of first order. On starting with pure A it is found that at the end of 10 minutes the total pressure of system is 176 mm. Hg and after a long time 270 mm Hg. From these data find (a) initial pressure of A (b) the pressure of A at the end of 10 minutes (c) the specific rate of reaction and (d) the half life period of the reaction?
- Q.42 The reaction $\text{AsH}_3(\text{g}) \longrightarrow \text{As}(\text{s}) + \frac{3}{2} \text{H}_2(\text{g})$ was followed at constant volume at 310°C by measuring the gas pressure at intervals Show from the following figures that reaction is of first order.
- | | | | | |
|------------------------|-----|-----|-----|-----|
| Time (in hrs) | 0 | 5 | 7.5 | 10 |
| Total pressure (in mm) | 758 | 827 | 856 | 882 |

Q.43 The decomposition of N_2O_5 according to the equation $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ is a first order reaction. After 30 min. from start of decomposition in a closed vessel the total pressure developed is found to be 284.5 mm Hg. On complete decomposition, the total pressure is 584.5 mm Hg. Calculate the rate constant of the reaction.

Q.44 The thermal decomposition of dimethyl ether as measured by finding the increase in pressure of the reaction



at 500°C is as follows:

Time (sec.)	390	1195	3155	∞
Pressure increase (mm Hg)	96	250	467	619

the initial pressure of ether was 312 mm Hg. Write the rate equation for this reaction and determine the rate constant of reaction.

Q.45 From the following data show that decomposition of H_2O_2 in aqueous solution is first order.

Time (in minutes)	0	10	20
Volume (in c.c. of KMnO_4)	22.8	13.3	8.25

Q.46 A definite volume of H_2O_2 under going spontaneous decomposition required 22.8 c.c. of standard permanganate solution for titration. After 10 and 20 minutes respectively the volumes of permanganate required were 13.8 and 8.25 c.c.

- Find order of reaction. How may the result be explained?
- Calculate the time required for the decomposition to be half completed.
- Calculate the fraction of H_2O_2 decomposed after 25 minutes.

Q.47 The following data were obtained in experiment on inversion of cane sugar.

Time (minutes)	0	60	120	180	360	∞
Angle of rotation (degree)	+13.1	+11.6	+10.2	+9.0	+5.87	-3.8

Show that the reaction is of first order. After what time would you expect a zero reading in polarimeter?

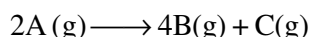
Q.48 In the hydrolysis of propyl acetate in the presence of dilute hydrochloric acid in dilute aqueous solution the following data were recorded :

Time from start in minutes	60	350
Percentage of ester decomposed	18.17	69.12

Calculate the time in which half the ester was decomposed.

Q.49 Hydrogen peroxide solution was stored in a mild steel vessel. It was found, however, that the hydrogen peroxide decomposed on the walls of the vessel (a first order reaction). An experiment with 100 ml of a solution gave 10.31 ml oxygen (corrected to N.T.P.) after 5.1 days under similar storage conditions. Find how long the peroxide can be stored before the loss of 20.00 ml oxygen occurs (per 100 ml solution) if complete decomposition of the sample to H_2O_2 gave 46.34 ml oxygen.

Q.50 The reaction given below, rate constant for disappearance of A is $7.48 \times 10^{-3} \text{ sec}^{-1}$. Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm to rise to 0.145 atm and also find the total pressure after 100 sec.



PARALLEL AND SEQUENTIAL REACTION

Q.51 For a reaction $\text{x} \begin{matrix} \xrightarrow{k_1} \text{y} \\ \xrightarrow{k_2} \text{z} \end{matrix}$, calculate value of ratio, $\frac{[\text{x}]_t}{[\text{y}] + [\text{z}]}$ at any given instant t.

- Q.52 $A \begin{matrix} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{matrix}$ $k_1 = x \text{ hr}^{-1}$; $k_1 : k_2 = 1 : 10$. Calculate $\frac{[C]}{[A]}$ after one hour from the start of the reaction. Assuming only A was present in the beginning.

- Q.53 A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as $A \begin{matrix} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{matrix}$; $k_1 = 1.26 \times 10^{-4} \text{ sec}^{-1}$ and $k_2 = 3.6 \times 10^{-5} \text{ sec}^{-1}$. Calculate the % distribution of B & C.

- Q.54 For a reaction $A \longrightarrow B \longrightarrow C$ $t_{1/2}$ for A & B are 4 and 2 minutes respectively. How much time would be required for the B to reach maximum concentration.

TEMPERATURE DEPENDENCE OF RATE (ACTIVATION ENERGY)

- Q.55 In gaseous reactions important for understanding the upper atmosphere, H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ at 500 K and $E_a = 77 \text{ kJ mol}^{-1}$, then calculate E_a for the bimolecular recombination of 2OH radicals to form H_2O & O at 500 K
- Q.56 The energy of activation of a first order reaction is $104.5 \text{ kJ mole}^{-1}$ and pre-exponential factor (A) is $5 \times 10^{13} \text{ sec}^{-1}$. At what temperature, will the reaction have a half life of 1 minute?
- Q.57 The specific rate constant for a reaction increases by a factor of 4, if the temperature is changed from 27°C to 47°C . Find the activation energy for the reaction.
- Q.58 The energy of activation and specific rate constant for a first order reaction at 25°C are 100 kJ/ mole and $3.46 \times 10^{-5} \text{ sec}^{-1}$ respectively. Determine the temperature at which half life of the reaction is 2 hours.
- $$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2(g)$$
- Q.59 A first order reaction is 50% complete in 30 minutes at 27°C and in 10 minutes at 47°C . Calculate the
- rate constant for the reaction at 27°C & 47°C and
 - energy of activation for the reaction.
- Q.60 A catalyst lowers the activation energy for a certain reaction from 75 kJ to 25 kJ mol^{-1} . What will be the effect on the rate of reaction at 25°C , after things being equal.
- Q.61 Given that the temperature coefficient for the saponification of ethyl acetate by NaOH is 1.75. Calculate activation energy for the saponification of ethyl acetate.

MECHANISM OF REACTION

- Q.62 The reaction $2NO + Br_2 \longrightarrow 2NOBr$, is supposed to follow the following mechanism

- $NO + Br_2 \xrightleftharpoons{\text{fast}} NOBr_2$
- $NOBr_2 + NO \xrightarrow{\text{slow}} 2NOBr$

Suggest the rate of law expression.

- Q.63 For the reaction $2H_2 + 2NO \longrightarrow N_2 + 2H_2O$, the following mechanism has been suggested:

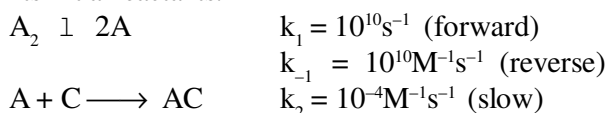
$2NO \rightleftharpoons N_2O_2$ equilibrium constant K_1 (fast)

$N_2O_2 + H_2 \xrightarrow{K_2} N_2O + H_2O$ (slow)

$N_2O + H_2 \xrightarrow{K_3} N_2 + H_2O$ (fast)

Establish the rate law for given reaction.

- Q.64 Write a stoichiometric equation for the reaction whose mechanism is detailed below. Determine the value of the equilibrium constant for the first step. Write a rate law equation for the overall reaction in terms of its initial reactants.



- Q.65 Reaction between NO and O₂ to form NO₂ is $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ follows the following mechanism
 $\text{NO} + \text{NO} \xrightleftharpoons[\text{K}_{-1}]{\text{K}_1} \text{N}_2\text{O}_2$ (in rapid equilibrium)
 $\text{N}_2\text{O}_2 + \text{O}_2 \xrightarrow{\text{K}_2} 2\text{NO}_2$ (slow)
 Show that the rate of reaction is given by $\frac{1}{2} \left(\frac{d[\text{NO}_2]}{dt} \right) = \text{K}[\text{NO}]^2[\text{O}_2]$
- Q.66 Deduce rate law expressions for the conversion of H₂ and I₂ to HI at 400°C corresponding to each of the following mechanisms:
- (a) $\text{H}_2 + \text{I}_2 \longrightarrow 2\text{HI}$ (one step)
- (b) $\text{I}_2 \rightleftharpoons 2\text{I}$
 $2\text{I} + \text{H}_2 \longrightarrow 2\text{HI}$ (slow)
- (c) $\text{I}_2 \rightleftharpoons 2\text{I}$
 $\text{I} + \text{H}_2 \rightleftharpoons \text{IH}_2$
 $\text{IH}_2 + \text{I} \longrightarrow 2\text{HI}$ (slow)
- (d) Can the observed rate law expression rate = k[H₂][I₂] distinguish among these mechanisms?
- (e) If it is known that ultraviolet light causes the reaction of H₂ and I₂ to proceed at 200°C with the same rate law expression, which of these mechanisms becomes most improbable? Are any of these mechanisms proved?

RADIOACTIVITY

- Q.67 Classify each of the following nuclides as "beta emitter", or "positron emitter":
 $^{49}_{20}\text{Ca}$ $^{195}_{80}\text{Hg}$ ^8_5B $^{150}_{67}\text{Ho}$ $^{30}_{13}\text{Al}$ $^{94}_{36}\text{Kr}$. Note: $^{200}_{80}\text{Hg}$ and $^{165}_{67}\text{Ho}$ are stable
- Q.68 Of the three isobars $^{114}_{48}\text{Cd}$ $^{114}_{49}\text{In}$ and $^{114}_{50}\text{Sn}$, which is likely to be radioactive? Explain your choice.
- Q.69 Complete the following nuclear equations:
- (a) $^{14}_7\text{N} + ^4_2\text{He} \rightarrow ^{17}_8\text{O} + \dots$ (b) $^9_4\text{Be} + ^4_2\text{He} \rightarrow ^{12}_6\text{C} + \dots$ (c) $^9_4\text{Be} (p, \alpha) \dots$
- (d) $^{30}_{15}\text{P} \rightarrow ^{30}_{14}\text{S} + \dots$ (e) $^3_1\text{H} \rightarrow ^3_2\text{He} + \dots$ (f) $^{43}_{20}\text{Ca} (\alpha, \dots) \rightarrow ^{46}_{21}\text{Sc}$
- Q.70 What symbol is needed to complete the nuclear equation $^{63}_{29}\text{Cu} (p, \dots) ^{62}_{29}\text{Cu}$?
- Q.71 Complete the following equations.
- (a) $^{23}_{11}\text{Na} + ^4_2\text{He} \rightarrow ^{26}_{12}\text{Mg} + ?$ (b) $^{64}_{29}\text{Cu} \rightarrow \beta^+ + ?$
- (c) $^{106}_{46}\text{Ag} \rightarrow ^{106}_{47}\text{Cd} + ?$ (d) $^{10}_5\text{B} + ^4_2\text{He} \rightarrow ^{13}_7\text{N} + ?$
- Q.72 How many α and β particle will be emitted when ^a_cX changes to ^b_dY ?
- Q.73 What is the α -activity in disintegration per minute 1 gm sample of ^{226}Ra . ($t_{1/2} = 1620$ year)
- Q.74 The half life of the nuclide Rn^{220} is 54.5 sec. What mass of radon is equivalent to 1 millicurie.
- Q.75 The activity of the radioactive sample drops to $\left(\frac{1}{64}\right)^{\text{th}}$ of its original value in 2 hr find the decay constant (λ).
- Q.76 $^{210}_{84}\text{Po}$ decays with α to $^{206}_{82}\text{Pb}$ with a half life of 138.4 days. If 1.0 gm of Po^{210} is placed in a closed tube, how much helium accumulate in 69.2 days at STP.
- Q.77 The half life period of $^{125}_{53}\text{I}$ is 60 days. What % of radioactivity would be present after 240 days.
- Q.78 At a certain instant a piece of radioactive material contains 10^{12} atoms. The half life of material is 30 days. Calculate the no. of disintegrations in one second.
- Q.79 Calculate the age of a vegetarian beverage whose tritium content is only 15% of the level in living plants. Given $t_{1/2}$ for $^3_1\text{H} = 12.3$ years.
- Q.80 A radioactive substance decays 20% in 10 min if at start there are 5×10^{20} atoms present, after what time will the number of atoms be reduced to 10^{18} atoms?

PROFICIENCY TEST

Q.1 Fill in the blanks with appropriate items :

- 1 Curie = _____ Bq.
- $^{14}_6\text{C}$ decays by emission of _____.
- Emission of a β -particle by a nuclide results in the formation _____ of the element.
- The number of α and β -particles emitted, when the following nuclear transformation takes place are _____ and _____ respectively.
$$^{238}_{92}\text{X} \longrightarrow ^{206}_{82}\text{Y}$$
- The nuclides with same difference of number of neutrons and number of protons are called _____.
- When $^{30}_{15}\text{P}$ emits a positron, the daughter nuclide formed is _____.
- A nuclide which lies above the zone of stability is likely to emit _____.
- ^3_1H and ^4_2He are _____.
- The half-life period of radioactive element if 87.5% of it disintegrates in 40 min is _____.
- For collision to be effective the energy possessed by the colliding molecules should be equal to or greater than the _____.
- In the reaction, $\text{H}_2 + \text{I}_2 \longrightarrow 2\text{HI}$, the rate of disappearance of H_2 is _____ the rate of appearance of HI .
- For an endothermic process, the minimum value of activation energy can be _____.
- The rate of a reaction is _____ to the collision frequency.
- The rate constant for the zero order reaction has the dimensions _____.
- The reactions with molecularity more than three are _____.
- A catalyst increases the rate of the reaction by _____ activation energy of reactants.
- If activation energy of reaction is low, it proceeds at _____ rate.
- In a multistep reaction, the _____ step is rate determining.
- Rate constant of a reaction, generally _____ with increase in temperature.
- The ratio $t_{7/8} / t_{1/2}$ for a first order reaction would be equal to _____.
- For a zero order reaction, the rate of the reaction is equal to the _____ of the reaction.
- The value of temperature coefficient is generally between _____.
- For a certain reaction, $x\text{M} \longrightarrow y\text{L}$, the rate of reaction increases by 4 times when the concentration of M is doubled. The rate law is _____.
- The rate equation $r = k [\text{A}][\text{B}]^{1/2}$ suggests that order of overall reaction is _____.
- A plot of $[\text{A}]$ vs t for a certain reaction $\text{A} \longrightarrow \text{B}$ with $r = k [\text{A}]^0$ will be a straight line with slope equal to _____.

26. $[E_{\text{activated complex}} - E_{\text{reactants}}] = \underline{\hspace{2cm}}$.
27. Among similar reactions, the endothermic reaction has activation energy than exothermic reaction.
28. For a order reaction the half-life ($t_{1/2}$) is independent of the initial conc. of the reactants.
29. For a first order reaction a graph of $\log [A]$ vs t has a slope equal to .
30. Average lifetime of a nuclei, $T_{\text{av}} = \underline{\hspace{2cm}} t_{1/2}$.

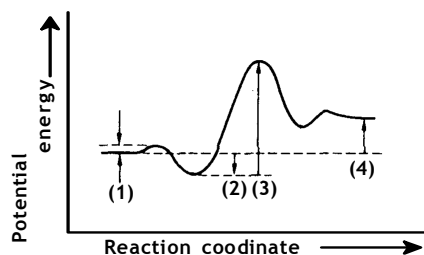
Q.2 True or False Statements :

1. Order of a reaction can be written from the balanced chemical equation.
2. For a reaction having order equal to $3/2$, the units for rate constant are sec^{-1} .
3. In a complex reaction the rate of overall reaction is governed by the slowest step.
4. $t_{1/2}$ for a first order reaction is 6.93 s, the value of rate constant for the reaction would be 10s^{-1} .
5. The ratio $t_{1/2} / t_{7/8}$ for a first order reaction is equal to $1/3$.
6. The rate of an exothermic reaction increases with the rise in temperature.
7. Molecularity of a reaction is always whole number.
8. The reactants which are thermodynamically unstable are always kinetically unstable also.
9. Order and molecularity of a single step reaction may or may not be same.
10. The activation energy of a catalysed reaction is more than the activation energy of the uncatalysed reaction.
11. For a zero order reaction $t_{3/4}$ is related to $t_{1/2}$ as $t_{3/4} = 1.5 t_{1/2}$
12. A nuclide having one proton and one neutron is represented as ${}^1_1\text{H}$.
13. A radioactive element decays by emitting one α and two β -particles. The daughter element formed is an isotope of the parent element.
14. The daughter product formed by the emission of α -particle has mass number less by 4 units than the parent nuclide.
15. ${}^{27}_{13}\text{Al}$ is a stable isotope while ${}^{29}_{13}\text{Al}$ is expected to disintegrate by β -emission.
16. Half-life period of a radioactive substance can be changed by using some suitable catalyst.
17. Emission of a β -particle by a radioactive nuclide results in decrease in N/P ratio.
18. Positron has same mass as that of an electron.
19. ${}^{14}_9\text{N}$ and ${}^{16}_8\text{O}$ are isotones.
20. The S.I. unit of activity is Curie (Ci).

EXERCISE -II

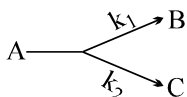
- Q.1 To investigate the decomposition of oxalic acid in concentrated H_2SO_4 at 50°C , a scientist prepared a $1/40 \text{ M}$ solution of oxalic acid in 99.5 percent H_2SO_4 , then removed aliquots at various reaction times t , and then determined the volumes v of a potassium permanganate solution required to react with a 10 ml portion. The results are given below :
- | | | | | | | | |
|-----------------|-------|------|------|------|------|------|------|
| t, min | 0 | 120 | 240 | 420 | 600 | 900 | 1440 |
| v, mL | 11.45 | 9.63 | 8.11 | 6.22 | 4.79 | 2.97 | 1.44 |
- Determine the reaction order with respect to oxalic acid and evaluate the specific rate constant.
- Q.2 A solution of A is mixed with an equal volume of a solution of B containing the same number of moles, and the reaction $\text{A} + \text{B} \rightarrow \text{C}$ occurs. At the end of 1h, A is 75 % reacted. How much of A will be left unreacted at the end of 2 h if the reaction is (a) first order in A and zero order in B; (b) first order in both A and B ; and (c) zero order in both A and B ?
- Q.3 The approach to the following equilibrium was observed kinetically from both directions:
 $\text{PtCl}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons [\text{Pt}(\text{H}_2\text{O})\text{Cl}_3]^- + \text{Cl}^-$ at 25°C , it was found that
- $$-\frac{\Delta}{\Delta t}[\text{PtCl}_4^{2-}] = [3.9 \times 10^{-5} \text{ sec}^{-1}][\text{PtCl}_4^{2-}] - [2.1 \times 10^{-3} \text{ L.mol}^{-1} \text{ sec}^{-1}][\text{Pt}(\text{H}_2\text{O})\text{Cl}_3^-][\text{Cl}^-]$$
- What is the value of equilibrium constant for the complexation of the fourth Cl^- by $\text{Pt}(\text{II})$?
- Q.4 The oxidation of certain metals is found to obey the equation $\tau^2 = \alpha t + \beta$ where τ is the thickness of the oxide film at time t , α and β are constants. What is the order of this reaction?
- Q.5 The complex $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$ reacts with water according to the equation.
 $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+} + \text{F}^-$
 The rate of the reaction = rate const. $\times [\text{complex}]^a [\text{H}^+]^b$. The reaction is acid catalysed i.e. $[\text{H}^+]$ does not change during the reaction. Thus rate = $k' [\text{Complex}]^a$ where $k' = k[\text{H}^+]^b$, calculate 'a' and 'b' given the following data at 25°C .
- | | | | |
|----------------------------|------------------------|--------------------|--------------------|
| $[\text{Complex}]\text{M}$ | $[\text{H}^+]\text{M}$ | $T_{1/2}\text{hr}$ | $T_{3/4}\text{hr}$ |
| 0.1 | 0.01 | 1 | 2 |
| 0.2 | 0.02 | 0.5 | 1 |
- Q.6 The reaction $\text{CH}_3\text{--CH}_2\text{--NO}_2 + \text{OH}^- \longrightarrow \text{CH}_3\text{--CH=NO}_2 + \text{H}_2\text{O}$ obeys the rate law for pseudo first order kinetics in the presence of a large excess of hydroxide ion. If 1% of nitro ethane undergoes reaction in half a minute when the reactant concentration is 0.002 M, What is the pseudo first order rate constant?
- Q.7 A flask containing a solution of N_2O_5 in CCl_4 was placed in a thermostat at 40°C . The N_2O_5 began to decompose by a first-order reaction, forming NO_2 and N_2O_4 , which remained in the solution, and oxygen, which defined pressure. The measurements were started ($t = 0$) when 10.75ml gas had collected. At $t = 2400 \text{ sec.}$, 29.65ml was measured. After a very long time, ($t = \infty$) 45.50ml was measured. Find the (a) rate constant, (b) half-life time for reaction at 40°C in CCl_4 solution. (c) What volume of gas should have collected after 4800 sec?
- Q.8 At room temperature (20°C) orange juice gets spoilt in about 64 hours. In a refrigerator at 3°C juice can be stored three times as long before it gets spoilt. Estimate (a) the activation energy of the reaction that causes the spoiling of juice. (b) How long should it take for juice to get spoilt at 40°C ?
- Q.9 A first order reaction, $\text{A} \rightarrow \text{B}$, requires activation energy of 70 kJ mol^{-1} . When a 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the percent decomposition in the same time in a 30% solution maintained at 40°C ? Assume that activation energy remains constant in this range of temperature.
- Q.10 Two reactions (i) $\text{A} \rightarrow \text{products}$ (ii) $\text{B} \rightarrow \text{products}$, follow first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310K. The half life for this reaction at 310K is 30 minutes. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300K.

Q.11 Choose the correct set of identifications.



- | | (1) | (2) | (3) | (4) |
|-----|--|--|--|--|
| (A) | ΔE for
$E + S \rightarrow ES$ | E_a for
$ES \rightarrow EP$ | $\Delta E_{\text{overall}}$
for $S \rightarrow P$ | E_a for
$EP \rightarrow E + P$ |
| (B) | E_a for
$E + S \rightarrow ES$ | ΔE for
$E + S \rightarrow ES$ | E_a for
$ES \rightarrow EP$ | $\Delta E_{\text{overall}}$
for $S \rightarrow P$ |
| (C) | E_a for
$ES \rightarrow EP$ | E_a for
$EP \rightarrow E + P$ | $\Delta E_{\text{overall}}$
for $S \rightarrow P$ | ΔE for
$EP \rightarrow E + P$ |
| (D) | E_a for
$E + S \rightarrow ES$ | E_a for
$ES \rightarrow EP$ | E_a for
$EP \rightarrow E + P$ | $\Delta E_{\text{overall}}$
for $S \rightarrow P$ |
| (E) | ΔE for
$E + S \rightarrow ES$ | $\Delta E_{\text{overall}}$
for $S \rightarrow P$ | ΔE for
$EP \rightarrow E + P$ | E_a for
$EP \rightarrow E + P$ |

Q.12 A certain organic compound A decomposes by two parallel first order mechanism

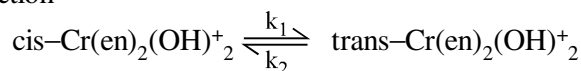


$$\text{If } k_1 : k_2 = 1 : 9 \text{ and } k_1 = 1.3 \times 10^{-5} \text{ s}^{-1}.$$

Calculate the concentration ratio of C to A, if an experiment is started with only A and allowed to run for one hour.

Q.13 Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as 20 volumes was left open. Due to this, some H_2O_2 decomposed. To determine the new volume strength after 6 hours, 10 mL of this solution was diluted to 100 mL. 10 mL of this diluted solution was titrated against 25 mL of 0.025 M KMnO_4 solution under acidic conditions. Calculate the rate constant for decomposition of H_2O_2 .

Q.14 The reaction



is first order in both directions. At 25°C the equilibrium constant is 0.16 and the rate constant k_1 is $3.3 \times 10^{-4} \text{ s}^{-1}$. In an experiment starting with the pure *cis* form, how long would it take for half the equilibrium amount of the *trans* isomer to be formed?

Q.15 A metal slowly forms an oxide film which completely protects the metal when the film thickness is 3.956 thousandths of an inch. If the film thickness is 1.281 thou. in 6 weeks, how much longer will it be before it is 2.481 thou.? The rate of film formation follows first order kinetics.

Q.16 An optically active compound A upon acid catalysed hydrolysis yield two optically active compound B and C by pseudo first order kinetics. The observed rotation of the mixture after 20 min was 5° while after completion of the reaction it was -20° . If optical rotation per mole of A, B & C are 60° , 40° & -80° . Calculate half life and average life of the reaction.

Q.17 A bacterial preparation was inactivated in a chemical bath. The inactivation process was found to be first order in bacterial concentration having rate constant $1.7 \times 10^{-2} \text{ sec}^{-1}$. Meanwhile the multiplication of bacteria ($1 \text{ bacterium} \rightarrow 2 \text{ bacteria}$) which also follows first order kinetics with rate constant $1.5 \times 10^{-3} \text{ sec}^{-1}$ also continued. Calculate the number of bacteria left after 2 minutes if the initial number of bacteria is 10^3 .

Q.18 The formation in water of *d*-potassium chromo-oxalate from its *l*-form is reversible reaction which is first order in both directions, the racemate being the equilibrium product. A polarimeter experiment at 22°C showed that, after 506 sec, 12 mole % of the *l*-isomer was converted to the *d*-form. Find the rate constant for the forward and the reverse reactions.

Q.19 For a reversible first-order reaction $A \xrightleftharpoons[k_2]{k_1} B$

$k_1 = 10^{-2} \text{ s}^{-1}$ and $[B]_{\text{eq}}/[A]_{\text{eq}} = 4$. If $[A]_0 = 0.01 \text{ mole L}^{-1}$ and $[B]_0 = 0$, what will be the concentration of B after 30 s ?

Q.20 For the reaction $A \xrightleftharpoons[k_{-1}]{k_1} P$. Following data is produced:

Time / Hr.	0	1	2	3	4	∞	
% A	100	72.5	56.8	45.6	39.5	30	Find k_1 , k_{-1} and K_{eq} .

Q.21 For the system $A_{(g)} \rightleftharpoons B_{(g)}$, ΔH for the forward reaction is -33 kJ/mol (Note : $\Delta H = \Delta E$ in this case).

Show that equilibrium constant $K = \frac{[B]}{[A]} = 5.572 \times 10^5$ at 300 K. If the activation energies E_f & E_b are in the ratio 20 : 31, calculate E_f and E_b at this temperature. Assume that the pre-exponential factor is the same for the forward and backward reactions.

Q.22 The conversion of A into B is an autocatalytic reaction $A \rightarrow B$ where B catalyzes the reaction. The rate equation is $-dx/dt = Kxy$ where x and y are concentrations of A and B at time t. Integrate this equation for initial concentrations x_0 and y_0 for A and B. Show that : $kt = \frac{2.303}{x_0 + y_0} \log \frac{x_0 y}{xy_0}$.

Q.23 A vessel contains dimethyl ether at a pressure of 0.4 atm. Dimethyl ether decomposes as $\text{CH}_3\text{OCH}_3(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g}) + \text{H}_2(\text{g})$. The rate constant of decomposition is $4.78 \times 10^{-3} \text{ min}^{-1}$. Calculate the ratio of initial rate of diffusion to rate of diffusion after 4.5 hours of initiation of decomposition. Assume the composition of gas present and composition of gas diffusing to be same.

Q.24(a) The reaction A proceeds in parallel channels $A \begin{matrix} \nearrow B \\ \searrow C \end{matrix}$ Although the $A \rightarrow C$ branch is thermodynamically more favorable than the branch $A \rightarrow B$, the product B may dominate in quantity over C. Why may this be so?

(b) In the above problem, suppose the half life values for the two branches are 60 minutes and 90 minutes, what is the overall half-life value?

Q.25 For the two parallel reactions $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$, show that the activation energy E' for the disappearance of A is given in terms of activation energies E_1 and E_2 for the two paths by

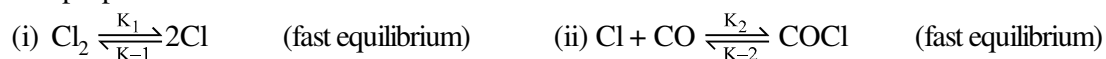
$$E' = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$$

Q.26 For the mechanism $A + B \xrightleftharpoons[k_2]{k_1} C \xrightarrow{k_3} D$

(a) Derive the rate law using the steady-state approximation to eliminate the concentration of C.

(b) Assuming that $k_3 \ll k_2$, express the pre-exponential factor A and E_a for the apparent second-order rate constant in terms of A_1, A_2 and A_3 and E_{a1}, E_{a2} and E_{a3} for the three steps.

Q.27 The reaction of formation of phosgene from CO and Cl_2 is $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$
The proposed mechanism is

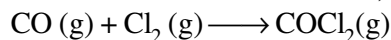


(iii) $\text{COCl} + \text{Cl}_2 \xrightarrow{k_3} \text{COCl}_2 + \text{Cl}$ (slow)

Show that the above mechanism leads to the following rate law $\frac{d[\text{COCl}_2]}{dt} = K[\text{CO}][\text{Cl}_2]^{3/2}$.

Where $K = k_3 \cdot \frac{k_2}{k_{-2}} \left(\frac{k_1}{k_{-1}} \right)^{1/2}$.

Q.28 The following kinetic data have been obtained at 250 °C, for the reaction



SET – 1

Initial Pressure CO = 400 Pa

Cl₂ = 800 × 10³ Pa

Time(sec) Pressure of COCl₂ (Pa)

0 0

2072 200

4140 300

10280 375

infinity 400

SET – 2

Initial Pressure CO = 1600 × 10³ Pa

Cl₂ = 400 Pa

Time(sec) Pressure of COCl₂ (Pa)

0 0

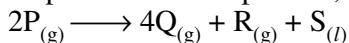
2070 300

4140 375

infinity 400

- Determine the order of reaction with respect to CO and Cl₂.
- Calculate the rate constant, when pressure in pascal and time in seconds.

Q.29 The decomposition of a compound P, at temperature T according to the equation

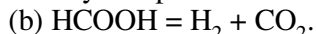
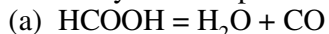


is the first order reaction. After 30 minutes from the start of decomposition in a closed vessel, the total pressure developed is found to be 317 mm Hg and after a long period of time the total pressure observed to be 617 mm Hg. Calculate the total pressure of the vessel after 75 minutes, if volume of liquid S is supposed to be negligible. Also calculate the time fraction $t_{7/8}$.

Given : Vapour pressure of S (l) at temperature T = 32.5 mm Hg.

Q.30 A certain reactant Bⁿ⁺ is getting converted to B⁽ⁿ⁺⁴⁾⁺ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing reagent which only reacts with Bⁿ⁺ and B⁽ⁿ⁺⁴⁾⁺. In this process, it converts Bⁿ⁺ to B⁽ⁿ⁻²⁾⁺ and B⁽ⁿ⁺⁴⁾⁺ to B⁽ⁿ⁻¹⁾⁺. At $t=0$, the volume of the reagent consumed is 25 ml and at $t = 10$ min, the volume used up is 32 ml. Calculate the rate constant of the conversion of Bⁿ⁺ to B⁽ⁿ⁺⁴⁾⁺ assuming it to be a first order reaction.

Q.31 The catalytic decomposition of formic acid may take place in two ways :



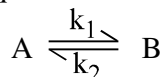
The rate constant and activation energy for reaction (a) are $2.79 \times 10^{-3} \text{ min}^{-1}$ at 236°C and 12.0 kcal mole⁻¹ respectively and for reaction (b) are $1.52 \times 10^{-4} \text{ min}^{-1}$ at 237°C and 24.5 kcal mole⁻¹ respectively. Find the temperature which will give a product made up of equimolar quantities of water vapour, carbon monoxide, hydrogen and carbon dioxide.

Q.32 The rate constant for the forward reaction $\text{A} \rightarrow \text{Product}$ is given by

$$\log k (\text{sec}^{-1}) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

and the rate constant for the reverse reaction is $1.2 \times 10^{-4} \text{ sec}^{-1}$ at 50°C. Calculate the value of maximum rate constant possible for the backward reaction. Given : Enthalpy of the reaction = -478 kJ/mol.

Q.33(a) The equilibrium between two isomers 'A' and 'B' can be represented as follow .



Where k_1 and k_2 are first order rate constants for forward and reverse reactions respectively. Starting with a non equilibrium mixture of conc. $[\text{A}]_0 = a$ and $[\text{B}]_0 = b$, it was found that 'x' mole of 'A' has

reacted after time 't'. Give an expression for rate, $\frac{dx}{dt}$, and hence show that integrated rate expression

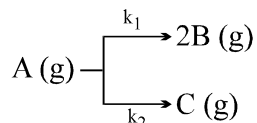
$$\text{is } \ln \left(\frac{P}{P-x} \right) = (k_1 + k_2) t \text{ where } P = \left(\frac{k_1 a - k_2 b}{k_1 + k_2} \right)$$

- After 69.3 minute $x = \frac{P}{2}$. Calculate k_1 and k_2 if equilibrium constant $K = 4$.
(Given : $\log 2 = 0.3010$)

- Q.34 The gaseous reaction : $n_1 A(g) \rightarrow n_2 B(g)$ is first order with respect to A. It is studied at a constant pressure, with a_0 as the initial amount of A. Show that the volume of system at the concentration of A at time 't' are given by the expressions

$$V = V_0 \left[\left(\frac{n_2}{n_1} \right) - \left(\frac{n_2}{n_1} - 1 \right) \exp(-n_1 kt) \right] ; [A]_t = [A]_0 \left[\frac{\exp(-n_1 kt)}{\left(\frac{n_2}{n_1} \right) - \left\{ \left(\frac{n_2}{n_1} \right) - 1 \right\} \exp(-n_1 kt)} \right]$$

- Q.35 For the following first order gaseous reaction



The initial pressure in a container of capacity V litres is 1 atm. Pressure at time $t = 10$ sec is 1.4 atm and after infinite time it becomes 1.5 atmosphere. Find the rate constant k_1 and k_2 for the appropriate reactions.

RADIOACTIVITY

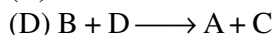
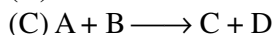
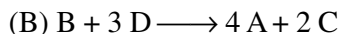
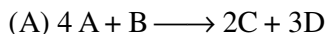
- Q.36 In a nature decay chain series starts with ${}_{90}\text{Th}^{232}$ and finally terminates at ${}_{82}\text{Pb}^{208}$. A thorium ore sample was found to contain 8×10^{-5} ml of helium at STP and 5×10^{-7} gm of Th^{232} . Find the age of ore sample assuming that source of He to be only due to decay of Th^{232} . Also assume complete retention of helium within the ore. (Half-life of $\text{Th}^{232} = 1.39 \times 10^{10}$ Y)
- Q.37 A 0.20 mL sample of a solution containing 1.0×10^{-7} Ci of ${}^3_1\text{H}$ is injected into the blood stream of a laboratory animal. After sufficient time for circulatory equilibrium to be established, 0.10 mL blood is found to have an activity of 20 dis/min. Calculate the blood volume of the animal.
- Q.38 A sample of ${}^{131}_{53}\text{I}$, as iodine ion, was administered to a patient in a carrier consisting of 0.10 mg of stable iodide ion. After 4.00 days, 67.7% of the initial radioactivity was detected in the thyroid gland of the patient. What mass of the stable iodide ion had migrated to the thyroid gland? ($t_{1/2} = 8$ days.)
- Q.39 Potassium having atomic mass = 39.1 u contains 93.10 atom % ${}^{39}\text{K}$, having atomic mass 38.96371 u; 0.0118 atom % ${}^{40}\text{K}$, which has mass of 40.0 u and is radioactive with $t_{1/2} = 1.3 \times 10^9$ y and 6.88 atom % ${}^{41}\text{K}$ having a mass of 40.96184 u. Calculate the specific activity of naturally occurring potassium.
- Q.40 A mixture of ${}^{239}\text{Pu}$ and ${}^{240}\text{Pu}$ has a specific activity of 6×10^9 dis/s/g. The half lives of the isotopes are 2.44×10^4 y and 6.08×10^3 y respectively. calculate the isotopic composition of this sample.
- Q.41 ${}_{92}\text{U}^{238}$ by successive radioactive decays changes to ${}_{82}\text{Pb}^{206}$. A sample of uranium ore was analyzed and found to contain 1.0 g of U^{238} and 0.1 g of Pb^{206} . Assuming that all the Pb^{206} had accumulated due to decay of U^{238} , find out the age of the ore. (Half life of $\text{U}^{238} = 4.5 \times 10^9$ years).
- Q.42 Fallout from nuclear explosions contains ${}^{131}\text{I}$ and ${}^{90}\text{Sr}$. Calculate the time required for the activity of each of these isotopes to fall to 1.0 % of its initial value. Radioiodine and radiostrontium tend to concentrate in the thyroid and the bones, respectively, of mammals which ingest them. Which isotope is likely to produce the more serious long-term effects? Half-life of ${}^{131}\text{I} = 8$ days, ${}^{90}\text{Sr} = 19.9$ yrs.
- Q.43 ${}^{218}_{84}\text{Po}$ ($t_{1/2} = 3.05$ min) decay to ${}^{214}_{82}\text{Pb}$ ($t_{1/2} = 2.68$ min) by α -emission, while Pb^{214} is a β -emitter. In an experiment starting with 1 gm atom of Pure Po^{218} , how much time would be required for the number of nuclei of ${}^{214}_{82}\text{Pb}$ to reach maximum.
- Q.44 A sample pitch blende is found to contain 50% Uranium and 2.425% Lead. Of this Lead only 93% was Pb^{206} isotope, if the disintegration constant is $1.52 \times 10^{-10} \text{ yr}^{-1}$. How old could be the pitch blende deposit.
- Q.45 A sample of Uraninite, a Uranium containing mineral was found on analysis to contain 0.214 gm of Pb^{206} for every gram of Uranium. Assuming that the lead all resulted from the radioactive disintegration of the Uranium since the geological formation of the Uraninite and all isotopes of Uranium other than ${}^{238}\text{U}$ can be neglected. Estimate the day when the mineral was formed in the Earth's crust. [$t_{1/2}$ of ${}^{238}\text{U} = 4.5 \times 10^9$ years]

EXERCISE -III

Q.1 The rate of a reaction is expressed in different ways as follows :

$$+\frac{1}{2} \frac{d[C]}{dt} = -\frac{1}{3} \frac{d[D]}{dt} = +\frac{1}{4} \frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

The reaction is:



Q.2 Units of rate constant for first and zero order reactions in terms of molarity M unit are respectively

- (A) sec^{-1} , M sec^{-1} (B) sec^{-1} , M (C) M sec^{-1} , sec^{-1} (D) M, sec^{-1}

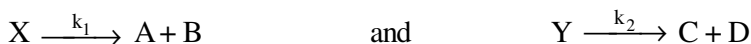
Q.3 The rate constant for the forward reaction $A(g) \rightleftharpoons 2B(g)$ is $1.5 \times 10^{-3} \text{ s}^{-1}$ at 100 K. If 10^{-5} moles of A and 100 moles of B are present in a 10 litre vessel at equilibrium then rate constant for the backward reaction at this temperature is

- (A) $1.50 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ (B) $1.5 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$
(C) $1.5 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ (D) 1.5×10^{-11}

Q.4 Reaction $A + B \longrightarrow C + D$ follow's following rate law : $\text{rate} = k = [A]^{\frac{1}{2}} [B]^{\frac{1}{2}}$. Starting with initial conc. of one mole of A and B each, what is the time taken for amount of A of become 0.25 mole. Given $k = 2.31 \times 10^{-3} \text{ sec}^{-1}$.

- (A) 300 sec. (B) 600 sec. (C) 900 sec. (D) none of these

Q.5 Consider the following first order competing reactions:



if 50% of the reaction of X was completed when 96% of the reaction of Y was completed, the ratio of their rate constants (k_2/k_1) is

- (A) 4.06 (B) 0.215 (C) 1.1 (D) 4.65

Q.6 A first order reaction is 50% completed in 20 minutes at 27°C and in 5 min at 47°C . The energy of activation of the reaction is

- (A) 43.85 kJ/mol (B) 55.14 kJ/mol (C) 11.97 kJ/mol (D) 6.65 kJ/mol

Q.7 For the first order reaction $A \longrightarrow B + C$, carried out at 27°C if $3.8 \times 10^{-16} \%$ of the reactant molecules exists in the activated state, the E_a (activation energy) of the reaction is

- (A) 12 kJ/mole (B) 831.4 kJ/mole (C) 100 kJ/mole (D) 88.57 kJ/mole

Q.8 The reactions of higher order are rare because

- (A) many body collisions involve very high activation energy
(B) many body collisions have a very low probability
(C) many body collisions are not energetically favoured.
(D) many body collisions can take place only in the gaseous phase.

EXERCISE-IV

OBJECTIVE PROBLEM

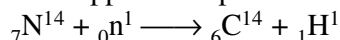
- Q.1 For a first order reaction
(A) the degree of dissociation is equal to $(1 - e^{-kt})$
(B) a plot of reciprocal concentration of the reactant vs time gives a straight line.
(C) the time taken for completion of 75% of reaction is thrice the $t_{1/2}$ of the reaction
(D) the pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1} . [JEE 1998]
- Q.2 The rate law for the reaction
 $\text{RCl} + \text{NaOH (aq)} \longrightarrow \text{ROH} + \text{NaCl}$ is given by $\text{Rate} = k[\text{RCl}]$. 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. [JEE 1998]
- Q.3 Which of the following statement(s) is (are) correct
(A) A plot of $\log K_p$ versus $1/T$ is linear
(B) A plot of $\log [X]$ versus time is linear for a first order reaction, $X \longrightarrow P$
(C) A plot of $\log P$ versus $1/T$ is linear at constant volume.
(D) A plot of P versus $1/V$ is linear at constant temperature. [JEE 1999]
- Q.4 The rate constant for the reaction [JEE SCR 2000]
 $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$
is $3.0 \times 10^{-5} \text{ sec}^{-1}$. If the rate is $2.4 \times 10^{-5} \text{ mol litre}^{-1} \text{ sec}^{-1}$, then the concentration of N_2O_5 (in mol litre^{-1}) is
(A) 1.4 (B) 1.2 (C) 0.004 (D) 0.8
- Q.5 If I is the intensity of absorbed light and C is the concentration of AB for the photochemical process
 $\text{AB} + h\nu \longrightarrow \text{AB}^*$, the rate of formation of AB^* is directly proportional to [JEE SCR 2001]
(A) C (B) I (C) I^2 (D) CI
- Q.6 Consider the chemical reaction, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$. The rate of this reaction can be expressed in terms of time derivative 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. [JEE SCR 2002]
(A) $\text{Rate} = -d[\text{N}_2]/dt = -1/3 d[\text{H}_2]/dt = 1/2 d[\text{NH}_3]/dt$
(B) $\text{Rate} = -d[\text{N}_2]/dt = -3 d[\text{H}_2]/dt = 2 d[\text{NH}_3]/dt$
(C) $\text{Rate} = d[\text{N}_2]/dt = 1/3 d[\text{H}_2]/dt = 1/2 d[\text{NH}_3]/dt$
(D) $\text{Rate} = -d[\text{N}_2]/dt = -d[\text{H}_2]/dt = d[\text{NH}_3]/dt$
- Q.7 In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in $2 \times 10^4 \text{ sec}$. The rate constant of reaction in sec^{-1} is [JEE SCR 2003]
(A) 2×10^4 (B) 3.45×10^{-5} (C) 1.3486×10^{-4} (D) 2×10^{-4}
- Q.8 The reaction, $X \longrightarrow \text{Product}$ 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
(A) $1.73 \times 10^{-4} \text{ M min}^{-1}$ (B) $3.47 \times 10^{-5} \text{ M min}^{-1}$
(C) $3.47 \times 10^{-4} \text{ M min}^{-1}$ (D) $1.73 \times 10^{-5} \text{ M min}^{-1}$ [JEE SCR 2004]
- Q.9 Which of the following statement is incorrect about order of reaction? [JEE 2005]
(A) Order of reaction is determined experimentally
(B) It is the sum of power of concentration terms in the rate law expression
(C) It does not necessarily depend on stoichiometric coefficients
(D) Order of the reaction can not have fractional value.

RADIOACTIVITY

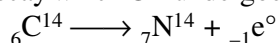
- Q.10 Loss of a β^- particle is equivalent to [JEE 1998]
(A) Increase of one proton only (B) Decrease of one neutron only
(C) Both (A) and (B) (D) None of these.
- Q.11 Decrease in atomic number is observed during [JEE 1998]
(A) α – emission (B) β^- – emission (C) Positron emission (D) Electron capture.
- Q.12 The number of neutrons accompanying the formation of ${}_{54}\text{X}^{139}$ and ${}_{38}\text{Sr}^{94}$ from the absorption of slow neutron by ${}_{92}\text{U}^{235}$ followed by nuclear fission is [JEE 1999]
(A) 0 (B) 2 (C) 1 (D) 3

Question No. 13 to 15 (3 questions)

Carbon 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 C^{14} undergoes.



The half life period of ${}^{14}\text{C}$ is 5770 years. The decay constant (λ) can be calculated by using the following

formula $\lambda = \frac{0.693}{t_{1/2}}$

The comparison of the β^- activity of the dead matter with that of 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} [JEE 2006]

- Q.13 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.
- Q.14 What should be the age of fossil for meaningful determination of its age?
(A) 6 years (B) 6000 years
(C) 60000 years (D) it can be used to calculate any age
- Q.15 A nuclear explosion has taken place leading to increase in concentration of C^{14} in nearby areas. C^{14} 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 the same
(D) $\frac{t_1}{t_2} = \frac{C_1}{C_2}$

SUBJECTIVE PROBLEM

Q.1(a) In the Arrhenius equation $k = A \exp(-E/RT)$, A may be termed as the rate constant at _____.

[JEE 1997]

(b) The rate constant for the first order decomposition of a certain reaction is described by the equation

$$\ln k \text{ (s}^{-1}\text{)} = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

(i) What is the energy of activation for this reaction?

(ii) The rate constant at 500 K.

(iii) At what temperature will its half life period be 256 minutes?

[JEE 1997]

(c) The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the pre exponential factor for the reaction is $3.56 \times 10^9 \text{ s}^{-1}$, calculate the rate constant at 318 K and also the energy of activation.

[JEE 1997]

(d) 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 the reaction after 1 h.

[JEE 1999]

Q.2 A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the 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^{-1} .

[JEE 2000]

Q.3 The rate of a first order reaction is $0.04 \text{ mole litre}^{-1} \text{ s}^{-1}$ at 10 minutes and $0.03 \text{ mol litre}^{-1} \text{ s}^{-1}$ at 20 minutes after initiation. Find the half life of the reaction.

[JEE 2001]

Q.4 $2X(g) \longrightarrow 3Y(g) + 2Z(g)$

Time (in Min)	0	100	200
---------------	---	-----	-----

Partial pressure of X	800	400	200
-----------------------	-----	-----	-----

(in mm of Hg)

Assuming ideal gas condition. Calculate

(a) Order of reaction

(b) Rate constant

(c) Time taken for 75% completion of reaction (d) Total pressure when $P_x = 700 \text{ mm}$. [JEE 2005]

RADIOACTIVITY

Q.5 ^{64}Cu (half-life = 12.8 hr) decays by β^- emission (38%), β^+ emission (19%) and electron capture (43%). Write the decay product and calculate partial half-lives for each of the decay processes. [JEE'2002]

Q.6 Fill in the blanks

(a) $^{235}_{92}\text{U} + {}^1_0\text{n} \longrightarrow {}^{137}_{52}\text{A} + {}^{97}_{40}\text{B} + \text{_____}$.

(b) $^{82}_{34}\text{Se} \longrightarrow 2 {}^0_{-1}\text{e} + \text{_____}$.

[JEE 2005]

ANSWER KEY

EXERCISE-I

RATE OF REACTION AND STOICHIOMETRIC COEFFICIENT

- Q.1 (a) $1 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$, (b) $3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
Q.2 (a) $0.019 \text{ mol L}^{-1} \text{ s}^{-1}$, (b) $0.037 \text{ mol L}^{-1} \text{ s}^{-1}$
Q.3 $2k_1 = k_2 = 4k_3$ Q.4 (i) $\frac{dx}{dt} = k[A][B]^2$, (ii) rate increases by 8 times
Q.5 rate increase by 27 times
Q.6 (i) $r = \frac{1}{4} \frac{d[\text{NO}]}{dt} = 9 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$, (ii) $36 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$, (iii) $54 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$
Q.7 (i) $7.2 \text{ mol litre}^{-1} \text{ min}^{-1}$, (ii) $7.2 \text{ mol litre}^{-1} \text{ min}^{-1}$ Q.8 1/6

ZERO ORDER

- Q.9 (i) 7.2 M, (ii) Think Q.10 $K = 0.01 \text{ M min}^{-1}$
Q.11 0.75 M Q.12 $6 \times 10^{-9} \text{ sec}$ Q.13 1.2 hr

FIRST ORDER

- Q.14 (i) 36 min., (ii) 108 min. Q.15 (i) 0.0223 min^{-1} , (ii) 62.17 min Q.17 924.362 sec
Q.18 expiry time = 41 months Q.19 $3.3 \times 10^{-4} \text{ s}^{-1}$ Q.20 $k = \frac{2.303}{t} \log \frac{1}{a}$ Q.21 11.2%

ORDER OF REACTION & RATE LAW

- Q.22 (a) Third order, (b) $r = k[\text{NO}]^2[\text{H}_2]$, (c) $8.85 \times 10^{-3} \text{ M sec}^{-1}$.
Q.23 (a) order w.r.t NO = 2 and w.r.t Cl_2 = 1, (b) $r = K[\text{NO}]^2[\text{Cl}_2]$, (c) $K = 8 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$, (d) rate = $0.256 \text{ mole L}^{-1} \text{ s}^{-1}$
Q.24 (i) first order (ii) $k = 1.308 \times 10^{-2} \text{ min}^{-1}$ (iii) 73%
Q.25 (i) rate = $[A][B]$; (ii) $k = 4 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$; (iii) rate = $2.8 \times 10^{-3} \text{ M} \cdot \text{s}^{-1}$
Q.26 (i) Zero order, (ii) $K = 5 \text{ Pa/s}$
Q.27 Zero order Q.28 (a) $n = 1$, (b) $\frac{dx}{dt} = k[\text{CH}_3\text{COCH}_3]$, (c) $8.67 \times 10^{-3} \text{ s}^{-1}$, (d) $1.56 \times 10^{-5} \text{ M s}^{-1}$

HALF LIFE

- Q.29 166.6 min Q.30 $4.62 \times 10^5 \text{ sec}$ Q.32 (i) $t = 13.96 \text{ hrs}$, (ii) 2.2176 litre
Q.33 54 min Q.34 15 min

CONCENTRATION REPLACED BY OTHER QUANTITIES IN FIRST ORDER

INTEGRATED RATE LAW

- Q.35 $k = \frac{1}{t} \ln \frac{P_3}{2(P_3 - P_2)}$ Q.36 $k = \frac{1}{t} \ln \frac{P_3}{(P_3 - P_2)}$
Q.37 $k = \frac{1}{t} \ln \frac{V_1}{(2V_1 - V_2)}$ Q.38 $k = \frac{1}{t} \ln \frac{4V_3}{5(V_3 - V_2)}$ Q.39 $k = \frac{1}{t} \ln \frac{r_\infty}{(r_\infty - r_t)}$
Q.40 $8.12 \times 10^{-6} \text{ Ms}^{-1}$, $0.012 \text{ atm min}^{-1}$

- Q.41 (a) 90 mm, (b) 47 mm, (c) 6.49×10^{-2} per minutes, (d) 10.677 min.
 Q.42 First order Q.43 $k_1 = 2.605 \times 10^{-3} \text{ min}^{-1}$
 Q.44 (i) $r = K[(\text{CH}_3)_2\text{O}]$, $0.000428 \text{ sec}^{-1}$ Q.45 First order
 Q.46 (a) first order, (b) 13.75 minutes, (c) 0.716
 Q.47 966 min Q.48 206.9 min Q.49 11.45 days
 Q.50 0.180 atm, 47.69 sec

PARALLEL AND SEQUENTIAL REACTION

- Q.51 $\frac{1}{e^{(K_1+K_2)t}-1}$ Q.52 $\frac{[C]}{[A]} = \frac{10}{11}(e^{11x}-1)$ Q.53 72.7, 22.3 Q.54 $t = 4 \text{ min}$

TEMPERATURE DEPENDENCE OF RATE (ACTIVATION ENERGY)

- Q.55 5 kJ mol^{-1} Q.56 349.1 k Q.57 $55.33 \text{ kJ mole}^{-1}$ Q.58 306 k
 Q.59 (a) $2.31 \times 10^{-12} \text{ min}^{-1}$, $6.93 \times 10^{-2} \text{ min}^{-1}$, (b) $43.85 \text{ kJ mole}^{-1}$
 Q.60 rate of reaction increases 5.81×10^8 times
 Q.61 $10.757 \text{ k cal mol}^{-1}$

MECHANISM OF REACTION

- Q.62 $r = K' [\text{NO}]^2 [\text{Br}_2]$ Q.63 $r = K [\text{NO}]^2 [\text{H}_2]$, where $K = k_2 \times K_1$
 Q.64 $k_{\text{eq}} = 1$, rate $= k_2 (\text{C}) (\text{A}_2)^{1/2}$ Q.66 (d) No, (e) mechanism (a) is incorrect

RADIOACTIVITY

- Q.67 beta emitter : ^{49}Ca , ^{30}Al , ^{94}Kr , positron emitter : ^{195}Hg , ^8B , ^{150}Ho
 Q.68 $^{114}_{49}\text{In}$, odd number of nucleons Q.69 (a) ^1_1H , (b) ^1_0n , (c) ^6_3Li , (d) $^0_{+1}\text{e}$, (e) $^0_{-1}\text{e}$, (f) p (proton)
 Q.70 d, deuteron Q.71 (a) ^1_1H (b) $^{64}_{28}\text{Ni}$ (c) $^0_{-1}\beta$ (d) ^1_0n
 Q.72 $\alpha = \frac{a-b}{4}$; $\beta = d + \frac{(a-b)}{2} - c$ Q.73 $2.16 \times 10^{12} \text{ events / min}$
 Q.74 $1.06 \times 10^{-15} \text{ kg}$ Q.75 $\lambda = 5.77 \times 10^{-4} \text{ sec}^{-1}$ Q.76 32 ml
 Q.77 6.25 % Q.78 $2.674 \times 10^5 \text{ dps}$ Q.79 33.67 years Q.80 4.65 hour

PROFICIENCY TEST

- Q.1**
- | | | | |
|---------------------------|--------------------------|--------------------------------------|----------------------------|
| 1. 3.7×10^{10} | 2. β -rays | 3. isobar | 4. 8, 6 |
| 5. isodiaphers | 6. $^{30}_{14}\text{Si}$ | 7. β -particles | 8. isotones |
| 9. 10 min. | 10. threshold energy | 11. half | 12. equal to ΔH |
| 13. directly proportional | | 14. $\text{mol L}^{-1}\text{s}^{-1}$ | 15. rare |
| 16. lowering | 17. faster | 18. slowest | 19. increases |
| 20. 3 | 21. rate constant | 22. 2 and 3 | 23. rate $= k[\text{M}]^2$ |
| 24. $1\frac{1}{2}$ | 25. $-k$ | 26. Activation energy | |
| 27. higher | 28. first | 29. $-\frac{k}{2.303}$ | 30. 1.44 |
- Q.2**
- | | | | |
|----------|-----------|-----------|-----------|
| 1. False | 2. False | 3. True | 4. False |
| 5. True | 6. True | 7. True | 8. False |
| 9. False | 10. False | 11. True | 12. False |
| 13. True | 14. True | 15. True | 16. False |
| 17. True | 18. True | 19. False | 20. False |

EXERCISE-II

- Q.1 First order, $k = 0.00144, 0.00144, 0.00145, 0.00145, 0.00150, 0.00140$, average 0.00145 min^{-1}
Q.2 (a) 6.25 ; (b) 14.3 ; (c) 0% Q.3 53.84 Q.4 $(d\tau/dt) = \alpha/2\tau$, -1 order
Q.5 $a = b = 1$ Q.6 $2 \times 10^{-2} \text{ min}^{-1}$
Q.7 (a) $3.27 \cdot 10^{-4} \text{ sec}^{-1}$; (b) 2120 sec; (c) 38.27 (measured : 55.00ml)
Q.8 (a) $43.46 \text{ kJ mol}^{-1}$, (b) 20.47 hour Q.9 % decomposition = 67.21%
Q.10 $k = 0.0327 \text{ min}^{-1}$ Q.11 B Q.12 0.537 Q.13 $k = 0.022 \text{ hr}^{-1}$
Q.14 4.83 mins Q.15 15.13 week Q.16 20 min, 28.66 min
Q.17 156 Q.18 $K_f = K_b = 0.00027 \text{ sec}^{-1}$ Q.19 0.0025 m
Q.20 $k = 9.74 \times 10^{-5} \text{ sec}^{-1}$, $k_{-1} = 4.18 \times 10^{-5} \text{ sec}^{-1}$ Q.21 $E_f = 6 \times 10^4 \text{ J}$; $E_b = 9.3 \times 10^4 \text{ J}$
Q.23 0.26 : 1 Q.24 (b) $t_{1/2} = 36 \text{ min}$
Q.26 (a) $\frac{d(D)}{dt} = \frac{k_1 k_3 (A)(B)}{k_2 + k_3}$; (b) $E_a = E_{a1} + E_{a3} - E_{a2}$, $A = \frac{A_1 A_3}{A_2}$
Q.28 Set - I : $3.5 \times 10^{-4} \text{ S}^{-1}$; Set - II : $6.7 \times 10^{-4} \text{ S}^{-1}$
Q.29 $P_t = 379.55 \text{ mm Hg}$, $t_{7/8} = 399.96 \text{ min}$ Q.30 0.0207 min^{-1}
Q.31 399°C ; $R = 1.987 \text{ Kcal. mol}^{-1} \text{ K}^{-1}$ Q.33 $k_2 = 2 \times 10^{-3} \text{ sec}^{-1}$, $k_1 = 8 \times 10^{-3} \text{ sec}^{-1}$
Q.35 0.805

RADIOACTIVITY

- Q.36 $t = 4.89 \times 10^9 \text{ years}$ Q.37 $V = 1.1 \text{ L}$ Q.38 0.0958 mg
Q.39 Specific activity = $30.69 \text{ dis. g}^{-1} \text{ s}^{-1}$ Q.40 $^{239}\text{Pu} = 45.1\%$, $^{240}\text{Pu} = 54.9\%$
Q.41 $t = 7.1 \times 10^8 \text{ years}$ Q.42 53.1 days, 132 yrs, ^{90}Sr is likely to be serious, the iodine will soon be gone
Q.43 4.125 min Q.44 $3.3 \times 10^8 \text{ years}$ Q.45 $1.4 \times 10^9 \text{ yrs}$

EXERCISE-III

- Q.1 B Q.2 A Q.3 D Q.4 B Q.5 D Q.6 B Q.7 C
Q.8 B Q.9 A Q.10 B Q.11 A Q.12 B Q.13 C Q.14 C
Q.15 A

EXERCISE-IV

OBJECTIVE PROBLEM

- Q.1 A, D Q.2 B Q.3 A, B, D Q.4 D Q.5 B
Q.6 A Q.7 C Q.8 C Q.9 D

RADIOACTIVITY

- Q.10 C Q.11 C, D Q.12 D Q.13 C Q.14 B
Q.15 A

SUBJECTIVE PROBLEM

- Q.1 (a) infinite temperature ; (b) (i) $2.50 \times 10^4 \text{ cal mol}^{-1}$, (ii) $2.35 \times 10^{-5} \text{ sec}^{-1}$, (iii) 513 ;
(c) $K_{318} = 9.2 \times 10^{-4} \text{ sec}^{-1}$, $E_a = 18.33 \text{ K cal mol}^{-1}$; (d) $A = 5.40 \times 10^{10} \text{ sec}^{-1}$, $E_a = 2.199 \times 10^4 \text{ J mol}^{-1}$
Q.2 100 kJ mol^{-1} Q.3 $t_{1/2} = 24.14 \text{ min}$ Q.4 (a) 1, (b) $6.93 \times 10^{-3} \text{ min}^{-1}$, (c) 200, (d) 950 mm

RADIOACTIVITY

- Q.5 $^{64}_{30}\text{Zn}$, $^{64}_{28}\text{Ni}$, $(t_{1/2})_1 = 33.68 \text{ hr}$, $(t_{1/2})_2 = 67.36 \text{ hr}$, $(t_{1/2})_3 = 29.76 \text{ hr}$ Q.6 (a) 2^1_0n , (b) $^{82}_{36}\text{Kr}$

STUDY PACKAGE

Target: IIT-JEE (Advanced)

SUBJECT: CHEMISTRY-XI

TOPIC: 10. Thermochemistry

Index:

- 1. Key Concepts**
- 2. Exercise I**
- 3. Exercise II**
- 4. Exercise III**
- 5. Exercise IV**
- 6. Answer Key**
- 7. 34 Yrs. Que. from IIT-JEE**
- 8. 10 Yrs. Que. from AIEEE**

EXERCISE I

Heat of reaction & it's type

- Q.1 When 2 moles of C_2H_6 are completely burnt 3120 kJ of heat is liberated . Calculate the heat of formation, ΔH_f° for C_2H_6 . Given ΔH_f° for $CO_2(g)$ & $H_2O(l)$ are -395 & -286 kJ respectively.
- Q.2 The standard heats of formation of $CH_4(g)$, $CO_2(g)$ and $H_2O(l)$ are -76.2 , -398.8 , -241.6 kJ mol $^{-1}$. Calculate amount of heat evolved by burning 1 m 3 of methane measured under normal (STP) conditions.
- Q.3 Calculate the enthalpy change when infinitely dilute solution of $CaCl_2$ and Na_2CO_3 mixed ΔH_f° for $Ca^{2+}(aq)$, $CO_3^{2-}(aq)$ and $CaCO_3(s)$ are -129.80 , -161.65 , -288.5 kcal mol $^{-1}$ respectively.
- Q.4 The enthalpies of neutralization of $NaOH$ & NH_4OH by HCl are -13680 calories and -12270 cal respectively . What would be the enthalpy change if one gram equivalent of $NaOH$ is added to one gram equivalent of NH_4Cl in solution ? Assume that NH_4OH and $NaCl$ are quantitatively obtained.
- Q.5 The heat of solution of anhydrous $CuSO_4$ is -15.9 kcal and that of $CuSO_4 \cdot 5H_2O$ is 2.8 kcal. Calculate the heat of hydration of $CuSO_4$.
- Q.6 The heat of reaction $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g)$ at $27^\circ C$ is -22.1 k cal . Calculate the heat of reaction at $77^\circ C$. The molar heat capacities at constant pressure at $27^\circ C$ for hydrogen , chlorine & HCl are 6.82 , 7.70 & 6.80 cal mol $^{-1}$ respectively.
- Q.7 Calculate standard heats of formation of carbon-di-sulphide (l) . Given the standard heat of combustion of carbon (s) , sulphur (s) & carbon-di-sulphide (l) are : -393.3 , -293.72 and -1108.76 kJ mol $^{-1}$ respectively.
- Q.8 A cylinder of gas supplied by a company contains 14 kg of butane . The heat of combustion of butane is 2658 kJ/mol . A normal family requires 20 MJ of energy per day of cooking. If the cylinder lasts for 26 days, what percentage of gas is wasted due to inefficient combustion.
- Q.9 The enthalpy change for the reaction $C_3H_8 + H_2(g) \longrightarrow C_2H_6(g) + CH_4(g)$ at $25^\circ C$ is -55.7 kJ/mol. Calculate the heat of combustion of $C_2H_6(g)$. The heats of combustion of H_2 , CH_4 & C_{graphite} are -285.8 , -890.0 & -393.5 kJ/mole respectively. Heat of combustion of propane is -2220 kJ mol $^{-1}$.
- Q.10 The standard enthalpy of neutralization of KOH with (a) HCN (b) HCl in dilute solution is -2480 cal . g eq $^{-1}$ and -13.68 kcal . g eq $^{-1}$ respectively . Find the enthalpy of dissociation of HCN at the same temperature.
- Q.11 At 300 K, the standard enthalpies of formation of $C_6H_5COOH(s)$, $CO_2(g)$ & $H_2O(l)$ are ; -408 , -393 & -286 KJ mol $^{-1}$ respectively . Calculate the heat of combustion of benzoic acid at:(i) constant pressure & (ii) constant volume.
- Q.12 The heat liberated on complete combustion of 7.8 g of benzene is 327 kJ . This heat has been measured at constant volume & at $27^\circ C$. Calculate the heat of combustion of benzene at constant pressure.

- Q.13 A cylinder of gas is assumed to contain 11.2 kg of butane. If a normal family needs 20,000 kJ of energy per day for cooking, how long will the cylinder last if the enthalpy of combustion, $\Delta H = -2658 \text{ kJ/mole}$ for butane.
- Q.14 The molar enthalpy of vaporization of benzene at its boiling point (353 K) is 30.84 kJmol^{-1} . What is the molar internal energy change? For how long would a 12 volt source need to supply a 0.5 A current in order to vaporise 7.8 g of the sample at its boiling point?
- Q.15 When 12.0 g of carbon reacted with oxygen to form CO & CO₂ at 25° C & constant pressure, 75.0 kcal of heat was liberated and no carbon remained. Calculate the mass of oxygen which reacted. $\Delta H_f^\circ(\text{CO}_2) = -95 \text{ kcal mol}^{-1}$, $\Delta H_f^\circ(\text{CO}) = -24 \text{ kcal mol}^{-1}$.
- Q.16 If the enthalpy of formation of HCl (g) and Cl⁻ (aq) are -92.3 kJ/mole and -167.44 kJ/mol , find the enthalpy of solution of hydrogen chloride gas.

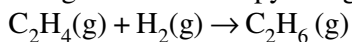
Calorimeter

- Q.17 0.16 g of methane was subjected to combustion at 27° C in a bomb calorimeter. The temperature of calorimeter system (including water) was found to rise by 0.5° C. Calculate the heat of combustion of methane at (i) constant volume (ii) constant pressure. The thermal capacity of calorimeter system is 17.7 kJ K^{-1} . ($R = 8.313 \text{ mol}^{-1} \text{ K}^{-1}$)
- Q.18 1.00 l sample of a mixture of CH₄(g) & O₂(g) measured at 25° C & 740 torr was allowed to react at constant pressure in a calorimeter which together with its contents had a heat capacity of 1260 cal/K. The complete combustion of the methane to CO₂ & H₂O caused a temperature rise in the calorimeter of 0.667 K. What was the mole percent of CH₄ in the original mixture? $\Delta H_{\text{comb}}^\circ(\text{CH}_4) = -215 \text{ kcal mol}^{-1}$.
- Q.19 Two solutions initially at 25° C were mixed in an adiabatic constant pressure calorimeter. One contains 400 ml of 0.2 M weak monoprotic acid solution. The other contains 100 ml of 0.80 M NaOH. After mixing temperature increased to 26.2 °C. How much heat is evolved in the neutralization of 1 mole of acid? Assume density of solution 1.0 g/cm^3 , and specific heat of solution $4.2 \text{ J/g}^\circ\text{C}$. Neglect heat capacity of the calorimeter.
- Q.20 When 1.0 g of fructose C₆H₁₂O₆(s) is burned in oxygen in a bomb calorimeter, the temperature of the calorimeter water increases by 1.56 °C. If the heat capacity of the calorimeter and its contents is $10.0 \text{ kJ/}^\circ\text{C}$. Calculate the enthalpy of combustion of fructose at 298 K.
- Q.21 A quantity of 1.92 g of methanol was burnt in a constant pressure calorimeter. The temperature of water increased by 4.2 °C. If the quantity of water surrounding the inner vessel was 2000 ml and the heat capacity of the inner vessel was $2.02 \text{ kJ/}^\circ\text{C}$. Calculate the heat of combustion of methanol. [Specific heat capacity of H₂O = $4.18 \text{ J/g}^\circ\text{C}$]

Bond energy

- Q.22 The enthalpy of dissociation of PH₃ is 954 kJ/mol and that of P₂H₄ is $1.485 \text{ MJ mol}^{-1}$. What is the bond enthalpy of the P–P bond?

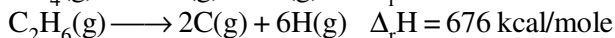
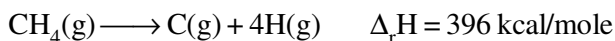
- Q.23 Using the bond enthalpy data given below, calculate the enthalpy change for the reaction.



Data:

Bond	C–C	C = C	C–H	H–H
Bond Enthalpy	336.81 KJ/mol	606.68 KJ/mol	410.87 KJ/mol	431.79 KJ/mol

- Q.24 The enthalpy change for the following process at 25°C and under constant pressure at 1 atm are as follows:



Calculate C–C bond energy in C_2H_6 & heat of formation of $\text{C}_2\text{H}_6(\text{g})$

Given: $\Delta_{\text{sub}} \text{C}(\text{s}) = 171.8 \text{ kcal/mole}$

B.E. (H–H) = 104.1 kcal/mole

- Q.25 The polymerisation of ethylene to linear polyethylene is represented by the reaction $n \text{CH}_2 = \text{CH}_2 \rightarrow (-\text{CH}_2 - \text{CH}_2)_n$ where n has a large integral value. Given that the average enthalpies of bond dissociation for C=C & C–C at 298 K are +590 & +331 KJ mol⁻¹ respectively. Calculate the enthalpy of polymerisation per mole of ethylene at 298 K.

- Q.26 From the following data :

Enthalpy of formation of $\text{CH}_3\text{CN} = 87.86 \text{ KJ/mol}$, Enthalpy of formation of $\text{C}_2\text{H}_6 = -83.68 \text{ KJ/mol}$

Enthalpy of sublimation of graphite = 719.65 KJ/mol

Enthalpy of dissociation of nitrogen = 945.58 KJ/mol ; Enthalpy of dissociation of $\text{H}_2 = 435.14 \text{ KJ/mol}$

C–H bond enthalpy = 414.22 KJ/mol

Calculate the (i) $\epsilon_{\text{C–C}}$; (ii) $\epsilon_{\text{C}\equiv\text{N}}$

- Q.27 The heat of combustion of acetylene is 312 kcal. If heat of formation of CO_2 & H_2O are –94.38 & –68.38 kcal respectively, calculate $\text{C}\equiv\text{C}$ bond energy. Given that heat of atomisation of C & H are 150.0 & 51.5 k cal respectively and C–H bond energy is 93.64 k cal.

- Q.28 Using the given data calculate enthalpy of formation of acetone (g). [All values in kJ mol⁻¹]

binding energy of : C–H = 413.4 ; C–C = 347.0 ; C=O = 728.0 ;

O=O = 495.0 ; H–H = 435.8 ; ΔH_{sub} of C = 718.4.

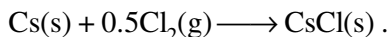
- Q.29 Find the enthalpy of S–S bond from the following data.



Born Haber cycle

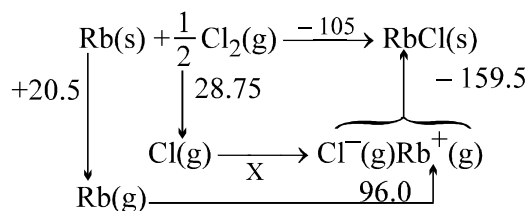
- Q.30 Calculate the electron affinity of fluorine atom using the following data. Make Born–Haber's cycle. All the values are in kJ mol⁻¹ at 25° C. $\Delta H_{\text{diss}}(\text{F}_2) = 160$, $\Delta H_f^\circ(\text{NaF}(\text{s})) = -571$, I.E. $[\text{Na}(\text{g})] = 494$, $\Delta H_{\text{vap}}[\text{Na}(\text{s})] = 101$. Lattice energy of $\text{NaF}(\text{s}) = -894$.

- Q.31 Cesium chloride is formed according to the following equation



The enthalpy of sublimation of Cs, enthalpy of dissociation of chlorine, ionization energy of Cs & electron affinity of chlorine are 81.2, 243.0, 375.7 and –348.3 kJ mol⁻¹. The energy change involved in the formation of CsCl is –388.6 kJ mol⁻¹. Calculate the lattice energy of CsCl .

Q.32 The Born-Haber cycle for rubidium chloride (RbCl) is given below (the energies are in k cal mol⁻¹)



Find out the electron affinity of chlorine in kJ mol⁻¹.

Resonance Energy

Q.33 The enthalpy of formation of ethane, ethylene and benzene from the gaseous atoms are -2839.2, -2275.2 and -5506 KJmol⁻¹ respectively. Calculate the resonance energy of benzene. The bond enthalpy of C-H bond is given as equal to + 410.87 KJ/mol.

Q.34 Calculate the heat of combustion of methyl alcohol at 298 K from the following data

Bond	C - H	C - O	O - H	O = O	C = O
Energy kJ mol ⁻¹	414	351.5	464.5	494	711

Resonance energy of CO₂ = -143 kJ mol⁻¹

Latent heat of vaporisation of methyl alcohol = 35.5 kJ mol⁻¹.

Latent heat of vaporisation of water = 40.6 kJ mol⁻¹.

Q.35 Calculate the enthalpy of combustion of benzene (l) on the basis of the following data :

- Resonance energy of benzene(l) = -152 kJ/mol
- Enthalpy of hydrogenation of cyclohexene(l) = -119 kJ/mol
- ΔH_f° of C₆H₁₂(l) = -156 kJ/mol
- ΔH_f° of H₂O(l) = -285.8 kJ/mol
- ΔH_f° of CO₂(g) = -393.5 kJ/mol

PROFICIENCY TEST

Q.1 Fill in the blanks with appropriate items:

1. The combustion of a substance is always _____.
2. If heat content of X is smaller than that of Y then the process $X \longrightarrow Y$ is _____.
3. $C(\text{Diamond}) \longrightarrow C(\text{Graphite}) + x \text{ kJ}$. The heat change in this process is called _____.
4. For any reaction, $\Delta H^\circ =$ _____.
5. As per reaction, $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) - 66 \text{ kJ}$ the value of ΔH_f of NO_2 is _____.
6. Heats of combustion of methane, carbon and hydrogen are -212 , -94 , $-68 \text{ kcal mol}^{-1}$. The heat of formation of CH_4 is _____.
7. The heat of neutralisation of 1 mole of $HClO_4$ with 1 gm-equivalent of $NaOH$ in aqueous solutions is _____ kJ mol^{-1} .
8. The heat of combustion of graphite and carbon monoxide respectively are $-393.5 \text{ kJ mol}^{-1}$ and -283 kJ mol^{-1} . Thus, heat of formation of carbon monoxide in kJ mol^{-1} is _____.
9. 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^{-1} . The value of enthalpy change for the reactions $H_2C = CH_2(g) + H_2(g) \longrightarrow H_3C - CH_3(g)$ at 298 K will be _____.
10. For the reaction,
 $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$
at constant temperature, $\Delta H - \Delta U$ is _____.

Q.2 Mark the following statements as True or False:

1. The ΔH of a reaction is independent of temperature.
2. The enthalpies of elements are always taken to be zero.
3. Integral heat of solution is same as heat of hydration of substance.
4. Heat of neutralisation of weak acid-strong base is not constant.
5. Combustion reactions are always exothermic.
6. Resonance energy is always negative.
7. $\Delta E = 0$ Combustion of benzene in a sealed container that is immersed in a water bath at 25°C and has rigid, thermally conducting walls.
8. For reaction $2A(g) + B(g) \longrightarrow 3C(g)$ $\Delta H = -x \text{ kJ}$
then for reaction $\frac{3}{2}C(g) \longrightarrow A(g) + \frac{B}{2}(g)$ $\Delta H = \frac{x}{2} \text{ kJ}$.
9. $\Delta H_f^\circ(C, \text{diamond}) \neq 0$.
10. For a particular reaction $\Delta E = \Delta H + P \cdot \Delta V$

EXERCISE II

- Q.1 Calculate the mass of mercury which can be liberated from HgO at 25°C by the treatment of excess HgO with 41.84 kJ of heat at
(a) constant pressure (b) constant volume conditions.
Given : ΔH_f° (HgO, s) = -90.8 kJ mol⁻¹ & M(Hg) = 200.6 g mol⁻¹.
- Q.2 For reduction of ferric oxide by hydrogen, $\text{Fe}_2\text{O}_3(\text{s}) + 3 \text{H}_2(\text{g}) \longrightarrow 2 \text{Fe}(\text{s}) + 3 \text{H}_2\text{O}(\text{l})$;
 $\Delta H_{298}^\circ = -35.1$ kJ. The reaction was found to be too exothermic to be convenient. It is desirable that ΔH° should be at the most -26 kJ. At what temperature is it possible?
 $C_p[\text{Fe}_2\text{O}_3] = 104.5$, $C_p[\text{Fe}(\text{s})] = 25.5$, $C_p[\text{H}_2\text{O}(\text{l})] = 75.3$, $C_p[\text{H}_2(\text{g})] = 28.9$ (all in J/mol)
- Q.3 From the following data of ΔH of the following reactions
 $\text{C}(\text{s}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{CO}(\text{g})$; $\Delta H = -110$ KJ
and $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$; $\Delta H = 132$ KJ
Calculate the mole composition of the mixture of steam and oxygen on being passed over coke at 1273 K, keeping the reaction temperature constant.
- Q.4 Although C_p is usually assumed to be constant, for more accurate calculations we must consider its variation with temperature as well. This relation is given by;
 $C_p = a + bT + cT^2 + dT^3$ cal mol⁻¹ K⁻¹.
- (a) Find the expression for the amount of heat required to raise the temperature of 1 mole of gas from T_1 K to T_2 K, while
(i) keeping the first term [i.e. $C_p = a$] (ii) keeping the first two terms.
(iii) keeping all the terms of the above expression. Note that each successive term introduces higher accuracy.
- (b) For CO_2 , $a = 5.0$, $b = 15 \times 10^{-5}$. Find the heat required to raise its temperature from 300 K to 500 K in case (i) and case (ii). (number of moles = 1). Case (ii) gives a more accurate value. Find the percent error in case (i).
- Q.5 An intimate mix of ferric oxide & Al is used as solid rocket fuel. Calculate the fuel value per gm & fuel value per CC of the mix. Heats of formation & densities are :
 $\Delta H_f^\circ (\text{Al}_2\text{O}_3) = -399$ k cal/mole ; $\Delta H_f^\circ (\text{Fe}_2\text{O}_3) = -199$ kcal / mole,
density of $\text{Fe}_2\text{O}_3 = 5.2$ g/cc ; density of Al = 2.7 g/cc.
- Q.6 A person takes 15 breaths per minute. The volume of air inhaled in each breath is 448 ml and contains 21% of oxygen by volume. The exhaled air contains 16% of oxygen by volume. If all the oxygen is used in the combustion of sucrose, how much of the latter is burnt in the body per day & how much heat is evolved. ΔH_{com} of sucrose is = -6000 kJ mol⁻¹. Take temperature to be 300 K throughout.
- Q.7 The enthalpies of neutralization of a strong acid HA & a weaker acid HB by NaOH are -13680 cal/equivalent & -2900 cal/equivalent respectively. When one equivalent of NaOH is added to a solution containing one equivalent of HA & one equivalent of HB, the enthalpy change was -6900 calories. In what ratio is the base distributed between HA & HB?
- Q.8 Calculate the heat produced when 3.785 litre of octane (C_8H_{18}) reacts with oxygen to form CO & water vapour at 25°C. The density of octane is 0.7025 gm/ml. Heat of combustion of C_8H_{18} is -1302.7 k cal/mol.
 $\Delta H_f^\circ \text{CO}_2(\text{g}) = -94.05$ k cal mol⁻¹ ; $\Delta H_f^\circ \text{CO}(\text{g}) = -26.41$ k cal mol⁻¹ ;
 $\Delta H_f^\circ \text{H}_2\text{O}(\text{l}) = -68.32$ k cal mol⁻¹ ; $\Delta H_f^\circ \text{H}_2\text{O}(\text{g}) = -57.79$ k cal mol⁻¹

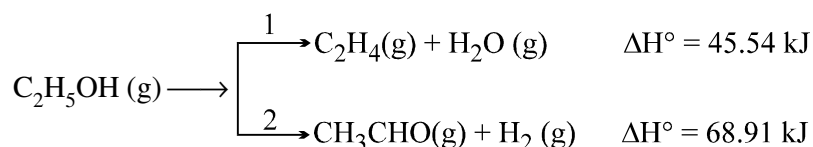
- Q.15 In the combustion of solid naphthalene ($C_{10}H_8$) at 298 K and atmospheric pressure 5157 kJ/mol of heat are evolved. Calculate resonance energy of naphthalene. Given
 Latent heat of sublimation of naphthalene = 72.0 kJ/mol
 Enthalpy of formation of $H_2O = -286.0 \text{ kJ mol}^{-1}$
 Enthalpy of formation of $CO_2 = -393.5 \text{ kJ mol}^{-1}$
 Enthalpy of atomization of C = $715.5 \text{ kJ mol}^{-1}$
 B.E. for C–C bond = $345.5 \text{ kJ mol}^{-1}$
 C = C bond = $617.0 \text{ kJ mol}^{-1}$
 C – H bond = $413.0 \text{ kJ mol}^{-1}$
 H–H bond = 436 kJ/mol
- Q.16 Calculate the proton affinity of $NH_3(g)$ from the following data (in kJ/mole)
 $\Delta H_{\text{dissociation}}^\circ : H_2(g) = 218$; $\Delta H_{\text{dissociation}}^\circ : Cl_2(g) = 124$
 $\Delta H_{\text{formation}}^\circ : NH_3(g) = -46$; $\Delta H_f^\circ : NH_4Cl(s) = -314$
 Lattice energy of $NH_4Cl(s) = -683$
 Ionization energy of H = 1310
 Electron affinity of Cl = 348
- Q.17 The standard enthalpy of formation of FeO & Fe_2O_3 is $-65 \text{ kcal mol}^{-1}$ and $-197 \text{ kcal mol}^{-1}$ respectively. A mixture of two oxides contains FeO & Fe_2O_3 in the mole ratio 2 : 1 . If by oxidation, it is changed into a 1 : 2 mole ratio mixture, how much of thermal energy will be released per mole of the initial mixture ?
- Q.18 The enthalpy of formation of $C_2H_5OH(l)$ is -66 kcal/mol . The enthalpy of combustion of CH_3-O-CH_3 is -348 kcal/mol . Given that the enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are -94 kcal/mol & -68 kcal/mol respectively, calculate ΔH for the isomerisation of ethanol to methoxymethane. All data are at 25°C .
- Q.19 During one of his adventures, Chacha Chaudhary got trapped in an underground cave which was sealed two hundred years back. The air inside was poisonous, having some amount of carbon monoxide in addition to O_2 and N_2 . Sabu, being huge, could not enter the cave. So, in order to save Chacha Chaudhary, he started sucking the poisonous air out of the cave by mouth. Each time he used to fill his lungs with cave air and exhale it out in the surroundings. In the meantime, fresh air from the surroundings effused into the cave till the pressure was again one atmosphere. Each time Sabu sucked out some air, the pressure in the cave dropped to half its initial value of one atmosphere.
 An initial sample of air taken from the cave measured 11.2 mL at STP and gave 7J on complete combustion at constant pressure.
- (i) If the safe level of CO in the atmosphere is less than 0.001 % by volume, how many times does Sabu need to suck out air in order to save Chacha Chaudhary?
- (ii) Sabu should rescue Chacha Chaudhary within 6 minutes else he will die. Precious 80 seconds are wasted in thinking of a way to rescue him. At maximum, how much time should each cycle of inhaling–exhaling take?
- $\Delta H_{\text{comb}}(CO) = -280 \text{ kJ} \cdot \text{mol}^{-1}$. Neglect any use of Graham's Law.

- Q.20 Fe_xO_4 a mixed oxide of iron consists of only Fe^{+2} & Fe^{+3} ions, with the ratio of $\text{Fe}^{+2} : \text{Fe}^{+3} = 1:2$ in the mixed oxide. From the data given below,
Enthalpy of formation, $\Delta H_f(\text{Fe}_x\text{O}_4) = -1092 \text{ kJ/mol}$.
Enthalpy of sublimation, $\Delta H_{\text{sub}}(\text{Fe}) = 390 \text{ kJ/mol}$.
B.D.E of $\text{O}_2 = 490 \text{ kJ/mol}$.
I.E₁ of Fe = 760 kJ/mol .
I.E₂ of Fe = 1560 kJ/mol .
I.E₃ of Fe = 2960 kJ/mol .
I.E₁ of $\text{O}^{2-} = -844 \text{ kJ/mol}$.
I.E₂ of $\text{O}^{2-} = 142 \text{ kJ/mol}$.
Lattice Energy of $\text{Fe}_x\text{O}_4 = 18930 \text{ kJ/mol}$.
Prove that value of x is 3 with the help of given data.

EXERCISE III

- Q.1 For which of the following change $\Delta H \neq \Delta E$?
(A) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \longrightarrow 2\text{HI}(\text{g})$ (B) $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \longrightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
(C) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$ (D) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$
- Q.2 $\Delta_r H$ of which of the following reactions is zero?
(A) $\text{H}_2(\text{g}) \longrightarrow 2\text{H}^+(\text{g}) + 2\text{e}^-$ (B) $2\text{H}(\text{g}) + \text{aq} \longrightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$
(C) $2\text{H}(\text{g}) \longrightarrow 2\text{H}^+(\text{g}) + 2\text{e}^-$ (D) $\text{H}_2(\text{g}) + \text{aq} \longrightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$
- Q.3 $\Delta_f H^\circ$ of water is $-285.8 \text{ kJ mol}^{-1}$. If enthalpy of neutralisation of monoacid strong base is $-57.3 \text{ kJ mol}^{-1}$, $\Delta_f H^\circ$ of OH^- ion will be
(A) $-228.5 \text{ kJ mol}^{-1}$ (B) $228.5 \text{ kJ mol}^{-1}$ (C) $114.25 \text{ kJ mol}^{-1}$ (D) $-114.25 \text{ kJ mol}^{-1}$
- Q.4 50.0 mL of 0.10 M HCl is mixed with 50.0 mL of 0.10 M NaOH. The solution temperature rises by 3.0°C . Calculate the enthalpy of neutralization per mole of HCl.
(A) $-2.5 \times 10^2 \text{ kJ}$ (B) $-1.3 \times 10^2 \text{ kJ}$ (C) $-8.4 \times 10^1 \text{ kJ}$ (D) $-6.3 \times 10^1 \text{ kJ}$
- Q.5 The enthalpy of neutralisation of a weak acid in 1 M solution with a strong base is $-56.1 \text{ kJ mol}^{-1}$. If the enthalpy of ionization of the acid is 1.5 kJ mol^{-1} and enthalpy of neutralization of the strong acid with a strong base is $-57.3 \text{ kJ equiv}^{-1}$, what is the % ionization of the weak acid in molar solution (assume the acid to be monobasic)?
(A) 10 (B) 15 (C) 20 (D) 25
- Q.6 For the allotropic change represented by the equation $\text{C}(\text{graphite}) \longrightarrow \text{C}(\text{diamond})$, $\Delta H = 1.9 \text{ kJ}$. If 6 g of diamond and 6 g of graphite are separately burnt to yield CO_2 , the heat liberated in first case is
(A) less than in the second case by 1.9 kJ (B) more than in the second case by 11.4 kJ
(C) more than in the second case by 0.95 kJ (D) less than in the second case by 11.4 kJ
- Q.7 If x_1 , x_2 and x_3 are enthalpies of H-H, O=O and O-H bonds respectively, and x_4 is the enthalpy of vaporisation of water, estimate the standard enthalpy of combustion of hydrogen
(A) $x_1 + \frac{x_2}{2} - 2x_3 + x_4$ (B) $x_1 + \frac{x_2}{2} - 2x_3 - x_4$ (C) $x_1 + \frac{x_2}{2} - x_3 + x_4$ (D) $2x_3 - x_1 - \frac{x_2}{2} - x_4$
- Q.8 $\text{NH}_3(\text{g}) + 3\text{Cl}_2(\text{g}) \rightleftharpoons \text{NCl}_3(\text{g}) + 3\text{HCl}(\text{g})$; $-\Delta H_1$
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$; ΔH_2
 $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$; ΔH_3
The heat of formation of $\text{NCl}_3(\text{g})$ in the terms of ΔH_1 , ΔH_2 and ΔH_3 is
(A) $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$ (B) $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$
(C) $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$ (D) None

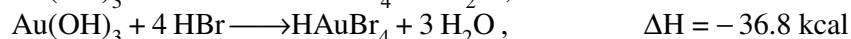
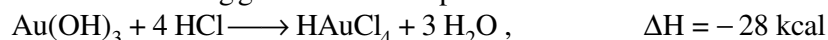
Q.9 Ethanol can undergoes decomposition to form two sets of products



if the molar ratio of C_2H_4 to CH_3CHO is 8 : 1 in a set of product gases, then the energy involved in the decomposition of 1 mole of ethanol is

- (A) 65.98 kJ (B) 48.137 kJ (C) 48.46 kJ (D) 57.22 kJ

Q.10 Reactions involving gold have been of particular interest to a chemist . Consider the following reactions,



In an experiment there was an absorption of 0.44 kcal when one mole of HAuBr_4 was mixed with 4 moles of HCl . What is the percentage conversion of HAuBr_4 into HAuCl_4 ?

- (A) 0.5 % (B) 0.6 % (C) 5 % (D) 50 %

Q.11 (i) Cis-2-butene \rightarrow trans-2-butene, ΔH_1

(ii) Cis-2-butene \rightarrow 1-butene, ΔH_2

(iii) Trans-2-butene is more stable than cis-2-butene.

(iv) Enthalpy of combustion of 1-butene, $\Delta H = -649.8 \text{ kcal/mol}$

(v) $9\Delta H_1 + 5\Delta H_2 = 0$

(vi) Enthalpy of combustion of trans-2-butene, $\Delta H = -647.0 \text{ kcal/mol}$.

The value of ΔH_1 & ΔH_2 in Kcal/mole are

- (A) -1.0, 1.8 (B) 1.8, -1.0 (C) -5, 9 (D) -2, 3.6

Q.12 The reaction $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g})$ has $\Delta H = -25 \text{ kCal}$.

Bond	Bond Energy kCal
$\text{E}_{\text{C}-\text{Cl}}$	84
$\text{E}_{\text{H}-\text{Cl}}$	103
$\text{E}_{\text{C}-\text{H}}$	x
$\text{E}_{\text{Cl}-\text{Cl}}$	y
$x : y = 9 : 5$	

From the given data, what is the bond energy of $\text{Cl}-\text{Cl}$ bond

- (A) 70 kCal (B) 80 kCal (C) 67.75 kCal (D) 57.75 kCal

Q.13 From the following data at 25°C

Reaction	$\Delta_f H^\circ$ kJ/mol
$\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{OH}(\text{g})$	42
$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{g})$	-242
$\text{H}_2(\text{g}) \longrightarrow 2\text{H}(\text{g})$	436
$\text{O}_2(\text{g}) \longrightarrow 2\text{O}(\text{g})$	495

Which of the following statement(s) is/are correct:

Statement (a) : $\Delta_f H^\circ$ for the reaction $\text{H}_2\text{O}(\text{g}) \longrightarrow 2\text{H}(\text{g}) + \text{O}(\text{g})$ is 925.5 kJ/mol

Statement (b) : $\Delta_f H^\circ$ for the reaction $\text{OH}(\text{g}) \longrightarrow \text{H}(\text{g}) + \text{O}(\text{g})$ is 502 kJ/mol

Statement (c) : Enthalpy of formation of $\text{H}(\text{g})$ is -218 kJ/mol

Statement (d) : Enthalpy of formation of $\text{OH}(\text{g})$ is 42 kJ/mol

(A) Statement c (B) Statement a, b, d (C) Statement b, c (D) Statement a, d

Q.14 A mixture of hydrogen gas and the theoretical amount of air at 25°C and a total pressure of 1 atm, is exploded in a **closed rigid vessel**. If the process occurs under **adiabatic condition** then using the given datas answer the questions that follow :

Given (i) $C_p = 8.3 \text{ cal deg}^{-1} \text{ mol}^{-1}$; (ii) $C_p = 11.3 \text{ cal deg}^{-1} \text{ mol}^{-1}$; $\Delta H_f [\text{H}_2\text{O}(\text{g})] = -57.8 \text{ Kcal}$

[Take air as 80% N_2 , 20% O_2 by volume]

(i) The value of C_p of N_2 & H_2O in the order $\text{N}_2, \text{H}_2\text{O}$ will be (in cal. $\text{deg}^{-1} \text{ mol}^{-1}$)

(A) 8.3, 8.3 (B) 8.3, 11.3 (C) 11.3, 11.3 (D) 11.3, 8.3

(ii) What will be the maximum temperature attained if the process occurs in adiabatic container.

(A) $\cong 2940 \text{ K}$ (B) $\cong 2665 \text{ K}$ (C) $\cong 1900 \text{ K}$ (D) $\cong 298 \text{ K}$

(iii) What will be the final pressure in atm.

(A) $\cong 8.5$ (B) $\cong 7.6$ (C) $\cong 5.46$ (D) $\cong 0.85$

(iv) If at initial temperature T_1 E_1 is initial internal energy & at higher final temperature. T_2 E_2 is the final internal energy, then which option is true

(A) $E_1 > E_2$

(B) $E_2 > E_1$

(C) $E_1 = E_2$

(D) can't be compared from the given data

Q.15 The commercial production of "Water gas" utilises the endothermic reaction $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{H}_2(\text{g}) + \text{CO}(\text{g})$. The heat required for this reaction is generated by combustion of coal to CO_2 using stoichiometric amount of air. (79% N_2 by volume and 21% O_2 by volume). The superheated steam undergoes 75% conversion. Using the following data, answer the question that follows :

$\Delta H_f [\text{CO}(\text{g})] = -110.53 \text{ kJ/mol}$; $\Delta H_f [\text{H}_2\text{O}(\text{g})] = -241.81 \text{ kJ/mol}$; $\Delta H_f [\text{CO}_2(\text{g})] = -314.0 \text{ kJ/mol}$

(i) The amount of heat liberated when one litre of product gases are burnt at 373 K and one atm is

(A) $\cong 3.6 \text{ kJ}$ (B) $\cong 3.9 \text{ kJ}$ (C) $\cong 4.43 \text{ kJ}$ (D) $\cong 5.34 \text{ kJ}$

(ii) Match the gas and percentage of each gas in one litre product gases.

Gas	Percentage
(I) N_2	(a) ≈ 23.1
(II) CO_2	(b) ≈ 36.4
(III) H_2	(c) ≈ 7.7
(IV) H_2O	(d) ≈ 9.7

(A) (I-a), (II-b), (III-c), (IV-d)

(B) (I-b), (II-a), (III-d), (IV-c)

(C) (I-c), (II-d), (III-a), (IV-c)

(D) (I-b), (II-d), (III-a), (IV-c)

EXERCISE IV

OBJECTIVE

- Q.1 Which of the following reactions defines ΔH_f° ?
(A) $C_{(\text{diamond})} + C_2(g) \longrightarrow CO_2(g)$ (B) $1/2 H_2(g) + 1/2 F_2(g) \longrightarrow HF(g)$
(C) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3$ (D) $CO(g) + 1/2 O_2(g) \longrightarrow CO_2(g)$ [JEE 2003]
- Q.2 ΔH_f° for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are -393.5 , -110.5 and $-241.8 \text{ kJ mol}^{-1}$ respectively. The standard enthalpy change (in kJ) for the reaction
 $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$ is
(A) 524.1 (B) 41.2 (C) -262.5 (D) -41.2 [JEE 2000]
- Q.3 Which of the following is not an endothermic reaction?
(A) Combustion of methane
(B) Decomposition of water
(C) Dehydrogenation of ethene to ethylene
(D) Conversion of graphite to diamond [JEE 1999]
- Q.4 Standard molar enthalpy of formation of CO_2 is equal to
(A) zero
(B) standard molar enthalpy of combustion of carbon (graphite)
(C) standard molar enthalpy of combustion of gaseous carbon
(D) sum of molar enthalpies of formation of CO and O_2 [JEE 1997]

SUBJECTIVE

- Q.5 Diborane is a potential rocket fuel which undergoes combustion according to the reaction,
 $B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$
From the following data, calculate the enthalpy change for the combustion of diborane :
 $2B(s) + \frac{3}{2} O_2(g) \longrightarrow B_2O_3(s); \quad \Delta H = -1273 \text{ kJ}$
 $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l); \quad \Delta H = -286 \text{ kJ}$
 $H_2O(l) \longrightarrow H_2O(g); \quad \Delta H = 44 \text{ kJ}$
 $2B(s) + 3H_2(g) \longrightarrow B_2H_6(g); \quad \Delta H = 36 \text{ kJ}$ [JEE 2000]
- Q.6 Estimate the average S–F bond energy in SF_6 . The ΔH_f° values of $SF_6(g)$, $S(g)$, and $F(g)$ are -1100 , 275 and 80 kJ/mol respectively. [JEE 99, 5]
- Q.7 From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of $CO_2(g)$, $H_2O(l)$ and propene (g) are -393.5 , -285.8 & 20.42 kJ/mol respectively. The enthalpy of isomerisation of cyclopropane to propene is -33.0 kJ/mol . [JEE '98, 5]
- Q.8 Compute the heat of formation of liquid methyl alcohol in kJ mol^{-1} , using the following data. Heat of vaporisation of liquid $CH_3OH = 38 \text{ kJ/mol}$. Heat of formation of gaseous atoms from the elements in their standard states; H, 218 kJ/mol ; C, 715 kJ/mol ; O, 249 kJ/mol .
Average Bond energies C–H, 415 kJ/mol ;
C–O, 356 kJ/mol ; O–H, 463 kJ/mol [JEE '97, 5]
- Q.9 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 km. What is the maximum distance a person will be able to walk after eating 120 g of glucose. [JEE '97, 2]

ANSWER KEY**EXERCISE I**

- Q.1 -88kJ/mol Q.2 35.973 MJ Q.3 2.95 kcal Q.4 -1410 cal
 Q.5 -18.7 kcal Q.6 -22.123 k cal Q.7 128.02 kJ Q.8 18.95 %
 Q.9 -1560.1 kJmol⁻¹ Q.10 11.2Kcal.
 Q.11 (i) -3201 kJ/mol ; (ii) -3199.75 kJ/mol Q.12 -3273.77 kJ/mol Q.13 25.66 days
 Q.14 $\Delta E = 27.91 \text{ KJ mol}^{-1}$, $t = 514 \text{ sec.}$
 Q.15 27.43 g O₂ Q.16 -75.14 kJ/mole Q.17 (i) -885 kJ/mol (ii) -889.980 kJ/mol
 Q.18 10.0 mol % CH₄ Q.19 -31.5 kJ/mole Q.20 -2808 kJ/mole Q.21 -726.6 kJ/mole
 Q.22 213 kJ / mol Q.23 -120.08 J/ml
 Q.24 B.E. (C-C) = 82 kcal/mole; $\Delta_f H[C_2H_6(g)] = -20.1 \text{ kcal/mole}$
 Q.25 -72 kJ mol⁻¹
 Q.26 (i) 343.08 ; (ii) 891.2 Q.27 $E_{C \equiv C} = 160.86 \text{ k cal}$
 Q.28 -192.3 kJ mol⁻¹ Q.29 277.5 kJ/mol Q.30 E.A. = -352 kJ mol⁻¹
 Q.31 -618.7 kJ mol⁻¹ Q.32 -90.75 kcal mol⁻¹
 Q.33 -23.68 KJ/mol Q.34 -669.7 kJ mol⁻¹
 Q.35 $H_f^\circ(\text{benzene}) = 49 \text{ kJ mol}^{-1}$, $H_C^\circ(\text{benzene}) = -3267.4 \text{ kJ mol}^{-1}$

PROFICIENCY TEST

- Q.1** 1. exothermic 2. endothermic 3. Heat of transition 4. $\sum v_p \Delta H^\circ_{(P)} - \sum v_r \Delta H^\circ_{(R)}$
 5. +33 kJ mol⁻¹ 6. -18 kcal mol⁻¹ 7. -57.2 kJ 8. -110.5
 9. -125.0 kJ 10. -3RT
Q.2 1. False 2. False 3. False 4. True 5. True
 6. True 7. False 8. True 9. True 10. False

EXERCISE II

- Q.1 (a) 92.435 g (b) 93.72 g Q.2 404 K Q.3 mole % $\text{O}_2(\text{g}) = 37.5$, $\text{H}_2\text{O}(\text{g}) = 62.5$
- Q.4 (a) (i) $a\Delta T$ (ii) $a\Delta T + \frac{b}{2}(T_2^2 - T_1^2)$ (b) 1000 cal, 1012 cal, 1.1858 % error
- Q.5 0.9346 k cal g^{-1} , 3.94 kcal cm^{-3} Q.6 9.822 MJ/day evolved
- Q.7 0.371 : 0.629 Q.8 $-666.81 \text{ k cal mol}^{-1}$, 15.55 Mcal
- Q.9 $\text{C}-\text{C} = 97.81 \text{ kJ}$, $\text{C}-\text{H} = 454.64 \text{ kJ}$, $\text{C}=\text{O} = 804.26 \text{ kJ}$, $\text{C}=\text{C} = 434.3 \text{ kJ}$, $\text{C}\equiv\text{C} = 733.48 \text{ kJ}$
- Q.10 +20.6 k cal Q.11 -154.68 k cal
- Q.12 292 kcal/mol Q.13 for $\text{Cl}^- -384 \text{ kJ mol}^{-1}$, for $\text{I}^- -307 \text{ kJ mol}^{-1}$
- Q.14 advantage = 5396 kJ mol^{-1} Q.15 $-287.0 \text{ kJ mol}^{-1}$ Q.16 -718 kJ/mol
- Q.17 Heat released = 13.4 kcal. per mol of initial mixture Q.18 22 kcal mol^{-1}
- Q.19 (i) 13 times, (ii) 21.53 sec

EXERCISE III

- Q.1 D Q.2 D Q.3 A Q.4 A Q.5 C Q.6 C Q.7 B
- Q.8 A Q.9 B Q.10 C Q.11 A Q.12 D Q.13 D
- Q.14 (i) B (ii) A (iii) A (iv) C Q.15 (i) A (ii) D

EXERCISE IV

- Q.1 B Q.2 B Q.3 A Q.4 B Q.5 $-2035 \text{ kJ mol}^{-1}$
- Q.6 309.6 kJ/mol Q.7 $-2091.32 \text{ kJ mol}^{-1}$ Q.8 -266 kJ mol^{-1}
- Q.9 4.82 km

STUDY PACKAGE

Target: IIT-JEE (Advanced)

SUBJECT: CHEMISTRY-XII

TOPIC: 11. Electrochemistry

Index:

- 1. Key Concepts**
- 2. Exercise I**
- 3. Exercise II**
- 4. Exercise III**
- 5. Exercise IV**
- 6. Answer Key**
- 7. 34 Yrs. Que. from IIT-JEE**
- 8. 10 Yrs. Que. from AIEEE**

KEY CONCEPTS

ELECTROCHEMICAL CELLS

An electrochemical cell consists of two electrodes (metallic conductors) in contact with an electrolyte (an ionic conductor).

An electrode and its electrolyte comprise an **Electrode Compartment**.

Electrochemical Cells can be classified as:

- (i) **Electrolytic Cells** in which a non-spontaneous reaction is driven by an external source of current.
- (ii) **Galvanic Cells** which produce electricity as a result of a spontaneous cell reaction

Note: In a **galvanic cell**, cathode is positive with respect to anode.

In a **electrolytic cell**, anode is made positive with respect to cathode.

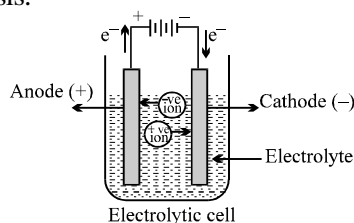
ELECTROLYSIS

The decomposition of electrolyte solution by passage of electric current, resulting into deposition of metals or liberation of gases at electrodes is known as electrolysis.

ELECTROLYTIC CELL

This cell converts electrical energy into chemical energy.

The entire assembly except that of the external battery is known as the electrolytic cell

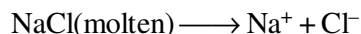


ELECTRODES

The metal strip at which positive current enters is called **anode**; anode is positively charged in electrolytic cell. On the other hand, the electrode at which current leaves is called **cathode**. Cathodes are negatively charged.

Anode	Positive	Loss of electron or oxidation takes place	Positive current enters
Cathode	Negative	Gain of electron or reduction takes place	Current leaves

ELECTROLYSIS OF MOLTEN SODIUM CHLORIDE

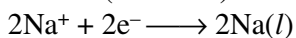


Reactions at

anode (oxidation)

:

cathode (reduction)



There are two types of electrodes used in the electrolytic cell, namely attackable and non-attackable. The attackable electrodes participate in the electrode reaction. They are made up of reactive metals like Zn, Cu, Ag etc. In such electrodes, atom of the metal gets oxidised into the corresponding cation, which is passed into the solution. Thus, such anodes get dissolved and their mass decreases. On the other hand, non-attackable electrodes do not participate in the electrode reaction as they are made up of unreactive elements like Pt, graphite etc. Such electrodes do not dissolve and their mass remains the same.

FARADAY'S LAWS OF ELECTROLYSIS:

(i) *First law of electrolysis :*

Amount of substance deposited or liberated at an electrode is directly proportional to amount of charge passed (utilized) through the solution.

$$w \propto Q$$

W = weight liberated, Q = charge in coulomb

$$w = ZQ$$

Z = electrochemical equivalent

when Q = 1 coulomb, then w = Z

Thus, weight deposited by 1 coulomb charge is called electrochemical equivalent.

Let 1 ampere current is passed till 't' seconds .

Then, $Q = It$ $\therefore w = ZIt$

1 Faraday = 96500 coulomb = Charge of one mole electrons

One faraday is the charge required to liberate or deposit one gm equivalent of a substance at corresponding electrode.

Let 'E' is equivalent weight then 'E' gm will be liberated by 96500 coulomb.

\therefore 1 Coulomb will liberate $\frac{E}{96500}$ gm ; By definition, $Z = \frac{E}{96500}$

$$\therefore W = \frac{ItE}{96500}$$

When a gas is evolved at an electrode, then above formula changes as,

$$V = \frac{ItV_e}{96500}$$

where V = volume of liberated gas, V_e = equivalent volume of gas.

Equivalent volume may be defined as:

The volume of gas liberated by 96500 coulomb at STP.

(ii) *Second law of electrolysis :*

When same amount of charge is passed through different electrolyte solutions connected in series then weight of substances deposited or dissolved at anode or cathode are in ratio of their equivalent weights. i.e. $w_1/w_2 = E_1/E_2$

QUALITATIVE ASPECTS OF ELECTROLYSIS

In the electrolysis process we have discussed above, we have taken molten salt as electrolyte, which contains only one cation and anion. Now, if the electrolyte taken contains more than one cation and anion (for example, aqueous solution of the ionic electrolyte), then the cation and anion that will get discharged depends on the ability of cation to get reduced and the ability of anion to get oxidised.

The ability of an ion to get oxidised or reduced depends upon the size, mass, positive charge, negative charge etc. Thus, it is not possible to predict qualitatively that which ion would be discharged first, as one factor might enhance the ability to discharge while the other factor may hamper it. This can only be predicted on the basis of quantitative value assigned based on the cumulative effect of all the factors responsible for an ion's ability to discharge. The value is referred as standard potential, which is determined by keeping the concentration of ion as 1 M, pressure of gas at 1 atm, and the measurement done at 25°C. For a cation, the standard reduction potential (SRP) values are compared. The cation having higher standard reduction potential value is discharged in preference to cation with lower SRP value provided the ions are at 1 M concentration. For an anion, the standard oxidation potential (SOP) values are compared and anion having higher SOP is preferentially discharged, if the concentration is 1 M for each of the ion. The SRP values at 25°C for some of the reduction half reactions are given in the table below.

S.NO.	Reduction half cell reaction	E° in volts at 25°C
1.	$F_2 + 2e^- \rightleftharpoons 2F^-$	+ 2.65
2.	$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+ 2.01
3.	$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+ 1.82
4.	$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightleftharpoons PbSO_4 + 2H_2O$	+ 1.65
5.	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+ 1.52
6.	$Au^{3+} + 3e^- \rightleftharpoons Au$	+ 1.50
7.	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+ 1.36
8.	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+ 1.33
9.	$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+ 1.229
10.	$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+ 1.07
11.	$NO_3^- + 4H^+ + 3e^- \rightleftharpoons NO + 2H_2O$	+ 0.96
12.	$2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+}$	+ 0.92
13.	$Cu^{2+} + I^- + e^- \rightleftharpoons CuI$	+ 0.86
14.	$Ag^+ + e^- \rightleftharpoons Ag$	+ 0.799
15.	$Hg_2^{2+} + 2e^- \rightleftharpoons 2 Hg$	+ 0.79
16.	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+ 0.77
17.	$I_2 + 2e^- \rightleftharpoons 2I^-$	+ 0.535
18.	$Cu^+ + e^- \rightleftharpoons Cu$	+ 0.53
19.	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+ 0.34
20.	$Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^-$	+ 0.27
21.	$AgCl + e^- \rightleftharpoons Ag + Cl^-$	+ 0.222
22.	$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+ 0.15
23.	$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+ 0.13
24.	$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
25.	$Fe^{3+} + 3e^- \rightleftharpoons Fe$	- 0.036
26.	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	- 0.126
27.	$Sn^{2+} + 2e^- \rightleftharpoons Sn$	- 0.14
28.	$AgI + e^- \rightleftharpoons Ag + I^-$	- 0.151
29.	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	- 0.25
30.	$Co^{2+} + 2e^- \rightleftharpoons Co$	- 0.28
31.	$Cd^{2+} + 2e^- \rightleftharpoons Cd$	- 0.403
32.	$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	- 0.41
33.	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	- 0.44
34.	$Cr^{3+} + 3e^- \rightleftharpoons Cr$	- 0.74
35.	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	- 0.762
36.	$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	- 0.828
37.	$Mn^{2+} + 2e^- \rightleftharpoons Mn$	- 1.18
38.	$Al^{3+} + 3e^- \rightleftharpoons Al$	- 1.66
39.	$H_2 + 2e^- \rightleftharpoons 2H^-$	- 2.25
40.	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	- 2.37
41.	$Na^+ + e^- \rightleftharpoons Na$	- 2.71
42.	$Ca^{2+} + e^- \rightleftharpoons Ca$	- 2.87
43.	$Ba^{2+} + 2e^- \rightleftharpoons Ba$	- 2.90
44.	$Cs^+ + e^- \rightleftharpoons Cs$	- 2.92
45.	$K^+ + e^- \rightleftharpoons K$	- 2.93
46.	$Li^+ + e^- \rightleftharpoons Li$	- 3.03

When solution of an electrolyte contains more than one type of cations and anions at concentrations different than 1 M, the discharge of an ion does not depend solely on standard potentials but also depends on the concentration of ion in the solution. This value is referred as potential, called as reduction potential for cation and oxidation potential for anion. The relation between reduction potential and standard reduction potential is given by Nernst equation, as

$$E_{RP} = E_{RP}^{\circ} - \frac{RT}{nF} \ln \frac{[\text{concentration of product}]}{[\text{concentration of reactant}]}$$

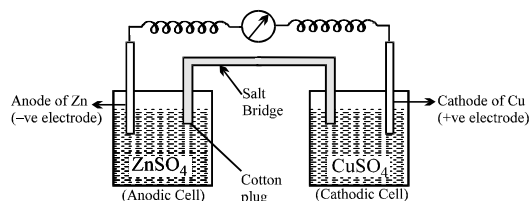
where E_{RP} = Reduction potential of cation and E_{RP}° = Standard reduction potential of cation.

Thus, it is possible that a cation (A^{+}) with lower standard reduction potential getting discharged in preference to cation (B^{+}) having higher standard reduction potential because their concentration might be such that the reduction potential of A^{+} is higher than that of B^{+} .

When two metal ions in the solution have identical values of their reduction potentials, the simultaneous deposition of both the metals will occur in the form of an alloy.

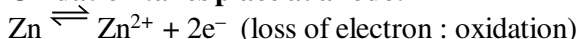
GALVANIC CELL

This cell converts chemical energy into electrical energy.

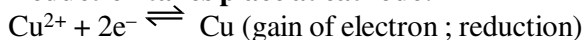


Galvanic cell is made up of two half cells i.e., anodic and cathodic. The cell reaction is of redox kind. Oxidation takes place at anode and reduction at cathode. It is also known as **voltaic cell**. It may be represented as shown in Fig. Zinc rod immersed in $ZnSO_4$ behaves as anode and copper rod immersed in $CuSO_4$ behaves as cathode.

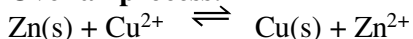
Oxidation takes place at anode:



Reduction takes place at cathode:



Over all process:



In galvanic cell like Daniell cell; electrons flow from anode (zinc rod) to the cathode (copper rod) through external circuit; zinc dissolves as Zn^{2+} ; Cu^{2+} ion in the cathode cell picks up two electron and become deposited at cathode.

SALT BRIDGE

Two electrolyte solutions in galvanic cells are separated using salt bridge as represented in the Fig. salt bridge is a device to minimize or eliminate the liquid junction potential. Saturated solution of salt like KCl, KNO_3 , NH_4Cl and NH_4NO_3 etc. in agar-agar gel is used in salt bridge. Salt bridge contains high concentration of ions viz. K^{+} and NO_3^{-} at the junction with electrolyte solution. Thus, salt bridge carries whole of the current across the boundary; more over the K^{+} and NO_3^{-} ions have same speed. Hence, salt bridge with uniform and same mobility of cations and anions minimize the liquid junction potential & completes the electrical circuit & permits the ions to migrate.

Representation of a cell (IUPAC conventions): Let us illustrate the convention taking the example of Daniel cell.

- (i) Anodic half cell is written on left and cathodic half cell on right hand side.

$$\text{Zn(s)} \mid \text{ZnSO}_4(\text{sol}) \parallel \text{CuSO}_4(\text{sol}) \mid \text{Cu(s)}$$
- (ii) Two half cells are separated by double vertical lines: Double vertical lines indicate salt bridge or any type of porous partition.
- (iii) EMF (electromotive force) may be written on the right hand side of the cell.
- (iv) Single vertical lines indicate the phase separation between electrode and electrolyte solution.

$$\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$$

(Illustration of Phase boundary)
- (v) Inert electrodes are represented in the bracket

$$\text{Zn} \mid \text{ZnSO}_4 \parallel \text{H}^+ \mid \text{H}_2, \text{Pt}$$

CONCEPT OF ELECTROMOTIVE FORCE (EMF) OF A CELL

Electron flows from anode to cathode in external circuit due to a pushing effect called or electromotive force (e.m.f.). E.m.f. is some times called as *cell potential*. Unit of e.m.f. of cell is volt.

EMF of cell may be calculated as :

$$E_{\text{cell}} = \text{reduction potential of cathode} - \text{Reduction potential of anode}$$

Similarly, standard e.m.f. of the cell (E°) may be calculated as

$$E^\circ_{\text{cell}} = \text{Standard reduction potential of cathode} - \text{Standard reduction potential of anode}$$

SIGN CONVENTION OF EMF

EMF of cell should be positive other wise it will not be feasible in the given direction .



NERNST EQUATION

Walter Nernst derived a relation between cell potential and concentration or Reaction quotient.

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \dots(1)$$

where ΔG and ΔG° are free energy and standard free energy change; 'Q' is reaction quotient.

Let n, Faraday charge is taken out from a cell of e.m.f. (E) then electrical work done by the cell may be calculated as,

$$\text{Work done} = \text{Charge} \times \text{Potential} = nFE$$

From thermodynamics we know that decrease in Gibbs free energy of a system is a measure of reversible or maximum obtainable work by the system if there is no work due to volume expansion

$$\therefore -\Delta G = nFE \quad \text{and} \quad -\Delta G^\circ = nFE^\circ$$

Thus from Eq. (i), we get $-nFE = -nFE^\circ + RT \ln Q$

$$\text{At } 25^\circ\text{C, above equation may be written as } E = E^\circ - \frac{0.0591}{n} \log Q$$

Where 'n' represents number of moles of electrons involved in process.

E, E° are e.m.f. and standard e.m.f. of the cell respectively.

In general, for a redox cell reaction involving the transference of n electrons

$aA + bB \longrightarrow cC + dD$, the EMF can be calculated as:

$$E_{\text{Cell}} = E^{\circ}_{\text{Cell}} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Prediction and feasibility of spontaneity of a cell reaction.

Work done by the cell = nFE ;

It is equivalent to decrease in free energy $\Delta G = -nFE$

Under standard state $\Delta G^{\circ} = -nFE^{\circ}$ (i)

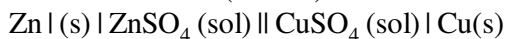
- (i) From thermodynamics we know, ΔG = negative for spontaneous process. Thus from eq.(i) it is clear that the EMF should be +ve for a cell process to be feasible or spontaneous.
- (ii) When ΔG = positive, E = negative and the cell process will be non spontaneous.
- (iii) When $G = 0$, $E = 0$ and the cell will attain the equilibrium.

Reactions	ΔG	E
Spontaneous	(-)	(+)
Non- spontaneous	(+)	(-)
Equilibrium	0	0

Standard free energy change of a cell may be calculated by electrode potential data.

Substituting the value of E° (i.e., standard reduction potential of cathode- standard reduction potential of anode) in eq. (i) we may get ΔG° .

Let us see whether the cell (Daniell) is feasible or not: i.e. whether Zinc will displace copper or not.



$$E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ volt} ; E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ volt}$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}}$$

$$= 0.34 - (-0.76) = +1.10 \text{ volt}$$

Since $E^{\circ} = +ve$, hence the cell will be feasible and zinc will displace copper from its salt solution. In other words zinc will reduce copper.

THERMODYNAMIC TREATMENT OF NERNST EQUATION

Determination of equilibrium constant : We know, that

$$E = E^{\circ} - \frac{0.0591}{n} \log Q \quad \text{..(i)}$$

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e. $E = 0$

\therefore From Eq. (i), we have

$$0 = E^{\circ} - \frac{0.0591}{n} \log K_{\text{eq}} \quad \text{or} \quad K_{\text{eq}} = \text{anti log} \left[\frac{nE^{\circ}}{0.0591} \right]$$

Heat of Reaction inside the cell: Let n Faraday charge flows out of a cell of e.m.f. E , then

$$-\Delta G = nFE \quad \text{(i)}$$

Gibbs Helmholtz equation (from thermodynamics) may be given as,

$$\Delta G = \Delta H + T \left[\frac{\partial \Delta G}{\partial T} \right]_p \quad \text{(ii)}$$

From Eqs. (i) and (ii), we have

$$-nFE = \Delta H + T \left[\frac{\partial (-nFE)}{\partial T} \right]_p = \Delta H - nFT \left[\frac{\partial E}{\partial T} \right]_p$$

$$\therefore \Delta H = -nFE + nFT \left[\frac{\partial E}{\partial T} \right]_p$$

Entropy change inside the cell : We know that $G = H - TS$ or $\Delta G = \Delta H - T\Delta S$... (i)
 where ΔG = Free energy change ; ΔH = Enthalpy change and ΔS = entropy change.
 According to Gibbs Helmholtz equation,

$$\Delta G = \Delta H + T \left[\frac{\partial \Delta G}{\partial T} \right]_p$$

$$\Delta G = \Delta H = T \left[\frac{\partial \Delta G}{\partial T} \right]_p$$

From Eqs. (i) and (ii), we have

$$-T\Delta S = T \left[\frac{\partial \Delta G}{\partial T} \right]_p \quad \text{or} \quad \Delta S = - \left[\frac{\partial \Delta G}{\partial T} \right]_p$$

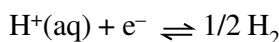
$$\text{or} \quad \Delta S = nF \left[\frac{\partial E}{\partial T} \right]_p$$

where $\left[\frac{\partial E}{\partial T} \right]_p$ is called temperature coefficient of cell e.m.f.

DIFFERENT TYPES OF HALF-CELLS AND THEIR REDUCTION POTENTIAL

(1) Gas-Ion Half Cell:

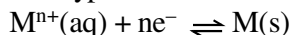
In such a half cell, an inert collector of electrons, platinum or graphite is in contact with gas and a solution containing a specified ion. One of the most important gas-ion half cell is the hydrogen-gas-hydrogen ion half cell. In this half cell, purified H_2 gas at a constant pressure is passed over a platinum electrode which is in contact with an acid solution.



$$E_{H^+/H_2} = E^0_{H^+/H_2} - \frac{0.0591}{1} \log \frac{(pH_2)^{1/2}}{[H^+]}$$

(2) Metal-Metal Ion Half Cell:

This type of cell consist of a metal M in contact with a solution containing M^{n+} ions.



$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

(3) Metal-Insoluble Salt - Anion Half Cell:

In this half cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt. eg. Silver-Silver Chloride Half Cell:

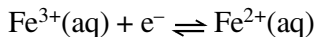
This half cell is represented as $Cl^-/AgCl/Ag$. The equilibrium reaction that occurs at the electrode is
 $AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$

$$E_{\text{Cl}^- / \text{AgCl} / \text{Ag}} = E^0_{\text{Cl}^- / \text{AgCl} / \text{Ag}} - \frac{0.0591}{1} \log [\text{Cl}^-]$$

potential of such cells depends upon the concentration of anions. Such cells can be used as **Reference Electrode**.

(4) Oxidation-reduction Half Cell:

This type of half cell is made by using an inert metal collector, usually platinum, immersed in a solution which contains two ions of the same element in different states of oxidation. eg. Fe^{2+} - Fe^{3+} half cell.



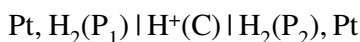
$$E_{\text{Fe}^{3+} / \text{Fe}^{2+}} = E^0_{\text{Fe}^{3+} / \text{Fe}^{2+}} - \frac{0.0591}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

CONCENTRATION CELL

The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cell.

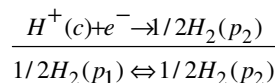
- (i) Electrode concentration cell
- (ii) Electrolyte concentration cell

Electrode Gas concentration cell :



Here, hydrogen gas is bubbled at two different partial pressures at electrode dipped in the solution of same electrolyte.

Cell process : $1/2\text{H}_2(\text{p}_1) \rightarrow \text{H}^+(\text{c}) + \text{e}^-$ (Anode process)

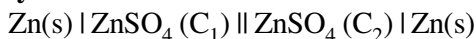


$$\therefore E = - \frac{2.303RT}{F} \log \left[\frac{\text{p}_2}{\text{p}_1} \right]^{1/2}$$

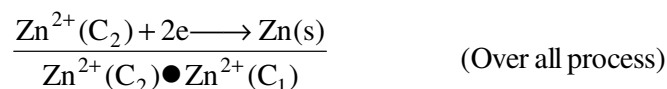
$$\text{or } E = \left[\frac{2.303RT}{2F} \right] \log \left[\frac{\text{p}_2}{\text{p}_1} \right], \text{ At } 25^\circ\text{C}, E = \frac{0.059}{2F} \log \left[\frac{\text{p}_1}{\text{p}_2} \right]$$

For spontaneity of such cell reaction, $\text{p}_1 > \text{p}_2$

Electrolyte concentration cells:



In such cells, concentration gradient arise in electrolyte solutions. Cell process may be given as,



\therefore From Nernst equation, we have

$$E = 0 - \frac{2.303RT}{2F} \log \left[\frac{C_1}{C_2} \right] \quad \text{or} \quad E = \frac{2.303RT}{2F} \log \left[\frac{C_2}{C_1} \right]$$

For spontaneity of such cell reaction, $C_2 > C_1$

CONDUCTANCE

Introduction:

Both metallic and electrolytic conductors obey Ohm's law

i.e. $V = IR$

where V = Potential difference in volt; I = Current in ampere ; R = resistance in Ohm

We know, resistance is directly proportional to length of conductor and inversely proportional to cross sectional area of the conductor.

$$R \propto \frac{l}{A} \quad \text{or} \quad R = \rho \frac{l}{A} \quad (\rho = \text{Specific resistance})$$

Specific resistance is the resistance of a conductor having lengths of 1 cm and cross sectional area of 1 cm².

Unit of R is ohm and unit of specific resistance is ohm cm

Reciprocal of resistance is called as *conductance* and reciprocal of specific resistance is called as *specific conductance*.

$$\frac{1}{R} = \frac{1}{\rho} \frac{A}{l} \quad \text{or} \quad C = K \frac{A}{l}$$

where C = conductance ohm⁻¹ ; K = specific conductance ohm⁻¹cm⁻¹ .

Mho and siemens are other units of conductance

$$K = \frac{l}{A} C$$

Specific conductance = Cell constant x Conductance

SPECIFIC CONDUCTANCE IS CONDUCTANCE OF 1 CM³ OF AN ELECTROLYTE SOLUTION.

In case of electrolytic solution, the specific conductance is defined as the conductance of a solution of definite concentration enclosed in a cell having two electrodes of unit area separated by 1 cm apart.

1. Equivalent Conductance

Equivalent conductance is the conductance of an electrolyte solution containing 1 gm equivalent of electrolyte. It is denoted by \wedge .

$$\wedge = K \times V$$

$$(\wedge = \text{ohm}^{-1} \text{ cm}^{-1} \times \text{cm}^3 = \text{ohm}^{-1} \text{ cm}^2)$$

Usually concentration of electrolyte solution is expressed as C gm equivalent per litre.

$$\text{Thus, } V = \frac{1000}{C}$$

$$\{\text{Volume having 1 gm equivalent electrolyte in the solution}\} \text{ Thus, } \wedge = K \times \frac{1000}{C}$$

2. Molar Conductance

Molar conductance may be defined as conductance of an electrolyte solution having 1 gm mole electrolyte in a litre. It is denoted by \wedge_m .

$$\wedge_m = K \times V$$

Usually concentration of electrolyte solution is expressed as ' M ' gm mole electrolyte per litre.

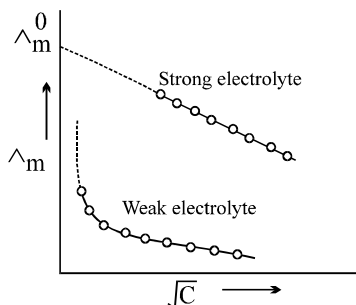
Thus,
$$V = \frac{1000}{M}$$

Hence,
$$\Lambda_m = K \times \frac{1000}{M}$$

Relation between Λ and Λ_m :
$$\Lambda_m = n \times \Lambda$$

DETERMINATION OF Λ_m^0 OR Λ^0

A plot of Λ_m vs \sqrt{C} as found experimentally is as shown below graphically.



The Λ_m vs \sqrt{C} plot of strong electrolyte being linear it can be extrapolated to zero concentration.

Thus, Λ_m values of the solution of the test electrolyte are determined at various concentrations the concentrations should be as low as good.

Λ_m values are then plotted against \sqrt{C} when a straight line is obtained. This is the extrapolated to zero concentration. The point where the straight line intersects Λ_m axis is Λ_m^0 of the strong electrolyte.

However, the plot in the case weak electrolyte being non linear, shooting up suddenly at some low concentration and assuming the shape of a straight line parallel to Λ_m axis. Hence extrapolation in this case is not possible. Thus, Λ_0 of a weak electrolyte cannot be determined experimentally. It can, however, be done with the help of Kohlrausch's law to be discussed later.

Kohlrausch's Law of Independent Migration of Ions

Kohlrausch determined Λ_0 values of pairs of some strong electrolytes containing same cation say KF and KCl, NaF and NaCl etc., and found that the difference in Λ_0 values in each case remains the same:

$$\Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{KF}) = \Lambda_m^0(\text{NaCl}) - \Lambda_m^0(\text{NaF})$$

He also determined Λ_0 values of pairs of strong electrolytes containing same anion say KF and NaF, KCl and NaCl etc. and found that the difference in Λ_0 values in each case remains the same.

$$\Lambda_m^0(\text{KF}) - \Lambda_m^0(\text{NaF}) = \Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{NaCl})$$

This experimental data led him to formulate the following law called Kohlrausch's law of independent migration of ions.

At infinite dilution when dissociation is complete, every ion makes some definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion which with it is associated and that the molar conductance at infinite dilution for any electrolyte is given by the sum of the contribution of the two ions. Thus,

$$\Lambda_m^0 = \lambda_+^0 + \lambda_-^0$$

Where λ_+^0 is the contribution of the cation and λ_-^0 is the contribution of the anion towards the molar conductance at infinite dilution. These contributions are called molar ionic conductances at infinite dilution. Thus, λ_+^0 is the molar ionic conductance of cation and λ_-^0 is the molar ionic conductance of anion, at infinite dilution. The above equation is, however, correct only for binary electrolyte like NaCl, MgSO_4 etc.

Application of Kohlrausch's law :

- (1) Determination of Λ_m^0 of a weak electrolyte:

In order to calculate Λ_m^0 of a weak electrolyte say CH_3COOH , we determine experimentally Λ_m^0 values of the following three strong electrolytes:

- (a) A strong electrolyte containing same cation as in the test electrolyte, say HCl
- (b) A strong electrolyte containing same anion as in the test electrolyte, say CH_3COONa
- (c) A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

Λ_m^0 of CH_3COOH is then given as:

$$\Lambda_m^0(\text{CH}_3\text{COOH}) = \Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{CH}_3\text{COONa}) - \Lambda_m^0(\text{NaCl})$$

Proof:

$$\Lambda_m^0(\text{HCl}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots\dots\dots(i)$$

$$\Lambda_m^0(\text{CH}_3\text{COONa}) = \lambda_{\text{CH}_3\text{COO}^-}^0 + \lambda_{\text{Na}^+}^0 \quad \dots\dots\dots(ii)$$

$$\Lambda_m^0(\text{NaCl}) = \lambda_{\text{Na}^+}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots\dots\dots(iii)$$

Adding equation (i) and equation (ii) and subtracting (iii) from them:

$$\Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{CH}_3\text{COONa}) - \Lambda_m^0(\text{NaCl}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{CH}_3\text{COO}^-}^0 = \Lambda_m^0(\text{CH}_3\text{COOH})$$

- (2) Determination of degree of dissociation (α):

$$\alpha = \frac{\text{No. of molecules ionised}}{\text{total number of molecules dissolved}} = \frac{\Lambda_m}{\Lambda_m^0}$$

- (3) Determination of solubility of sparingly soluble salt

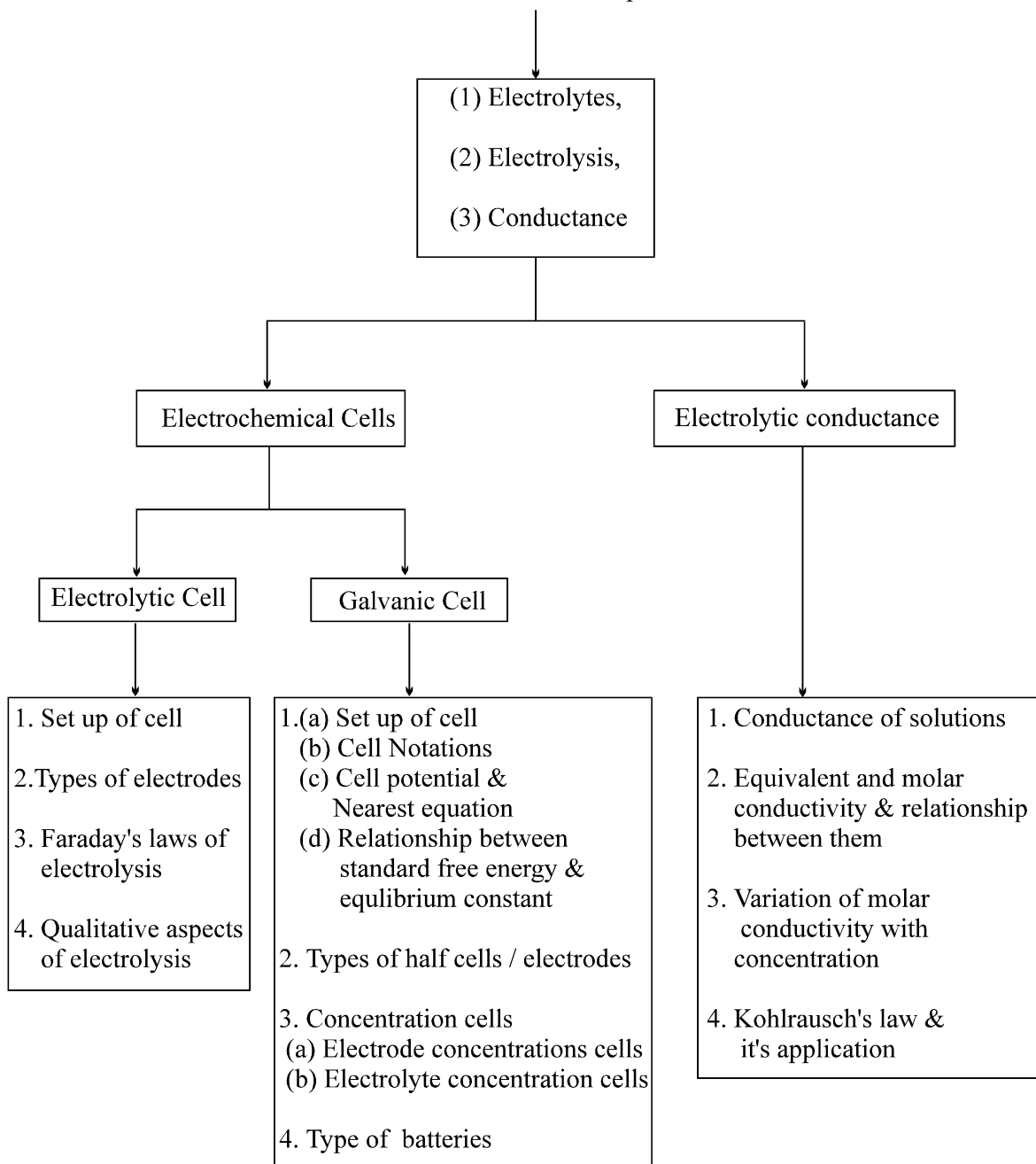
The specific conductivity of a saturated solution of the test electrolyte (sparingly soluble) made in conductivity water is determined by the method as described above. From this the specific conductivity of conductivity water is deducted. The molar conductance of the saturated solution is taken to be equal to Λ_m^0 as the saturated solution of a sparingly soluble salt is extremely dilute. Hence from equation (4).

$$\Lambda_m^0 = \frac{1000\kappa}{C},$$

where C is the molarity of solution and hence the solubility.

ATLAS

Some Basic Concept



EASY RIDE

ELECTROLYTIC CELL :

- Q.1 Calculate the no. of electrons lost or gained during electrolysis of
(a) 3.55 gm of Cl^- ions (b) 1 gm Cu^{2+} ions (c) 2.7 gm of Al^{3+} ions
- Q.2 How many faradays of electricity are involved in each of the case
(a) 0.25 mole Al^{3+} is converted to Al.
(b) 27.6 gm of SO_3 is converted to SO_3^{2-}
(c) The Cu^{2+} in 1100 ml of 0.5 M Cu^{2+} is converted to Cu.
- Q.3 0.5 mole of electron is passed through two electrolytic cells in series. One contains silver ions, and the other zinc ions. Assume that only cathode reaction in each cell is the reduction of the ion to the metal. How many gm of each metals will be deposited.
- Q.4 The electrosynthesis of MnO_2 is carried out from a solution of MnSO_4 in H_2SO_4 (aq). If a current of 25.5 ampere is used with a current efficiency of 85%, how long would it take to produce 1 kg of MnO_2 ?
- Q.5 A constant current of 30 A is passed through an aqueous solution of NaCl for a time of 1.0 hr. How many grams of NaOH are produced? What is volume of Cl_2 gas at S.T.P. produced?
- Q.6 If 0.224 litre of H_2 gas is formed at the cathode, how much O_2 gas is formed at the anode under identical conditions?
- Q.7 If 0.224 litre of H_2 gas is formed at the cathode of one cell at S.T.P., how much of Mg is formed at the cathode of the other electrolytic cell.
- Q.8 Assume 96500 C as one unit of electricity. If cost of electricity of producing x gm Al is Rs x, what is the cost of electricity of producing x gm Mg?
- Q.9 Chromium metal can be plated out from an acidic solution containing CrO_3 according to following equation:
 $\text{CrO}_3(\text{aq}) + 6\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow \text{Cr}(\text{s}) + 3\text{H}_2\text{O}$
Calculate :
(i) How many grams of chromium will be plated out by 24000 coulombs and
(ii) How long will it take to plate out 1.5 gm of chromium by using 12.5 ampere current
- Q.10 Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50 percent. If the potential drop across the cell is 3.0 volts, how much energy will be consumed?
- Q.11 How long a current of 2A has to be passed through a solution of AgNO_3 to coat a metal surface of 80cm^2 with $5\mu\text{m}$ thick layer? Density of silver = 10.8g/cm^3 .
- Q.12 3A current was passed through an aqueous solution of an unknown salt of Pd for 1Hr. 2.977g of Pd^{m} was deposited at cathode. Find n.
- Q.13 50mL of 0.1M CuSO_4 solution is electrolyzed with a current of 0.965 A for a period of 200 sec. The reactions at electrodes are:
Cathode : $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$ Anode : $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$
Assuming no change in volume during electrolysis, calculate the molar concentration of Cu^{2+} , H^+ and SO_4^{2-} at the end of electrolysis.
- Q.14 A metal is known to form fluoride MF_2 . When 10A of electricity is passed through a molten salt for 330 sec., 1.95g of metal is deposited. Find the atomic weight of M. What will be the quantity of electricity required to deposit the same mass of Cu from CuSO_4 ?

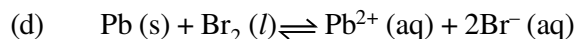
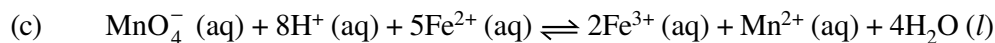
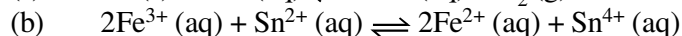
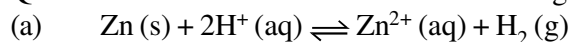
- Q.15 10g fairly concentrated solution of CuSO_4 is electrolyzed using 0.01F of electricity. Calculate:
 (a) The weight of resulting solution (b) Equivalents of acid or alkali in the solution.
- Q.16 An electric current is passed through electrolytic cells in series one containing $\text{Ag}(\text{NO}_3)(\text{aq.})$ and other $\text{H}_2\text{SO}_4(\text{aq.})$. What volume of O_2 measured at 25°C and 750mm Hg pressure would be liberated from H_2SO_4 if
 (a) one mole of Ag^+ is deposited from AgNO_3 solution
 (b) 8×10^{22} ions of Ag^+ are deposited from AgNO_3 solution.
- Q.17 Cadmium amalgam is prepared by electrolysis of a solution of CdCl_2 using a mercury cathode. How long should a current of 5A be passed in order to prepare 12% Cd–Hg amalgam on a cathode of 2gm Hg ($\text{Cd}=112.4$)
- Q.18 After electrolysis of NaCl solution with inert electrodes for a certain period of time. 600 mL of the solution was left. Which was found to be 1N in NaOH. During the same time, 31.75 g of Cu was deposited in the copper voltameter in series with the electrolytic cell. Calculate the percentage yield of NaOH obtained.
- Q.19 Three electrolytic cells A, B, C containing solution of ZnSO_4 , AgNO_3 and CuSO_4 , respectively are connected in series. A steady current of 2 ampere was passed through them until 1.08 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and of zinc were deposited?
- Q.20 Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 minutes. It was found that after electrolysis the concentration of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the original solution.
- Q.21 A solution of $\text{Ni}(\text{NO}_3)_2$ is electrolysed between platinum electrodes using a current of 5 ampere for 20 mintue. What mass of Ni is deposited at the cathode?
- Q.22 A current of 3.7A is passed for 6hrs. between Ni electrodes in 0.5L of 2M solution of $\text{Ni}(\text{NO}_3)_2$. What will be the molarity of solution at the end of electrolysis?

GALVANIC CELL :

Representation of Cell diagrams, complete and half cell reactions :

- Q.23 Make complete cell diagrams of the following cell reactions :
- $\text{Cd}^{2+}(\text{aq}) + \text{Zn}(\text{s}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Cd}(\text{s})$
 - $2\text{Ag}^+(\text{aq}) + \text{H}_2(\text{g}) \rightleftharpoons 2\text{H}^+(\text{aq}) + 2\text{Ag}(\text{s})$
 - $\text{Hg}_2\text{Cl}_2(\text{s}) + \text{Cu}(\text{s}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) + 2\text{Hg}(\text{l})$
 - $\text{Cr}_2\text{O}_7^{2-}(\text{aq.}) + 14\text{H}^+(\text{aq}) + 6\text{Fe}^{2+}(\text{aq}) \rightleftharpoons 6\text{Fe}^{3+}(\text{aq}) + 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$
- Q.24 Write cell reaction of the following cells :
- $\text{Ag} | \text{Ag}^+(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu}$
 - $\text{Pt} | \text{Fe}^{2+}, \text{Fe}^{3+} || \text{MnO}_4^-, \text{Mn}^{2+}, \text{H}^+ | \text{Pt}$
 - $\text{Pt}, \text{Cl}_2 | \text{Cl}^-(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag}$
 - $\text{Pt}, \text{H}_2 | \text{H}^+(\text{aq}) || \text{Cd}^{2+}(\text{aq}) | \text{Cd}$

Q.25 Write half cells of each cell with following cell reactions :

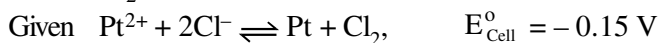
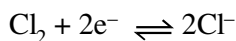


Electrode potential and standard electrode potential :

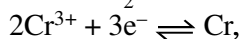
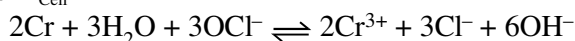
Q.26 For the cell reaction $2\text{Ce}^{4+} + \text{Co} \rightleftharpoons 2\text{Ce}^{3+} + \text{Co}^{2+}$

E°_{cell} is 1.89 V. If $E^\circ_{\text{Co}^{2+}|\text{Co}}$ is -0.28 V, what is the value of $E^\circ_{\text{Ce}^{4+}|\text{Ce}^{3+}}$?

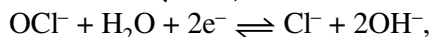
Q.27 Determine the standard reduction potential for the half reaction :



Q.28 What is E°_{cell} if



$$E^\circ = -0.74 \text{ V}$$



$$E^\circ = 0.94 \text{ V}$$

ΔG° , E°_{cell} and K_{eq} :

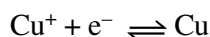
Q.29 Is 1.0 M H^+ solution under H_2SO_4 at 1.0 atm capable of oxidising silver metal in the presence of 1.0 M Ag^+ ion?

$$E^\circ_{\text{Ag}^+|\text{Ag}} = 0.80 \text{ V}, \quad E^\circ_{\text{H}^+|\text{H}_2(\text{Pt})} = 0.0 \text{ V}$$

Q.30 If for the half cell reactions $\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+$ $E^\circ = 0.15$ V



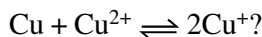
Calculate E° of the half cell reaction



also predict whether Cu^+ undergoes disproportionation or not.

Q.31 If $E^\circ_{\text{Fe}^{2+}|\text{Fe}} = -0.44$ V, $E^\circ_{\text{Fe}^{3+}|\text{Fe}^{2+}} = 0.77$ V. Calculate $E^\circ_{\text{Fe}^{3+}|\text{Fe}}$.

Q.32 If $E^\circ_{\text{Cu}^+|\text{Cu}} = 0.52$ V, $E^\circ_{\text{Cu}^{2+}|\text{Cu}} = 0.34$ V, what is E°_{cell} of the cell reaction



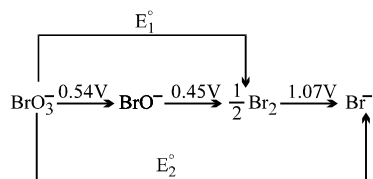
is cell reaction spontaneous?

Q.33 Calculate the EMF of a Daniel cell when the concentration of ZnSO_4 and CuSO_4 are 0.001 M and 0.1M respectively. The standard potential of the cell is 1.1V.

Q.34 Calculate the equilibrium constant for the reaction $\text{Fe} + \text{CuSO}_4 \rightleftharpoons \text{FeSO}_4 + \text{Cu}$ at 25°C .

Given $E^\circ(\text{Fe}/\text{Fe}^{2+}) = 0.44\text{V}$, $E^\circ(\text{Cu}/\text{Cu}^{2+}) = -0.337\text{V}$.

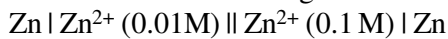
- Q.35 For a cell $\text{Mg(s)} \mid \text{Mg}^{2+}(\text{aq}) \parallel \text{Ag}^+(\text{aq}) \mid \text{Ag}$, Calculate the equilibrium constant at 25°C . Also find the maximum work that can be obtained by operating the cell.
 $E^\circ (\text{Mg}^{2+}/\text{Mg}) = -2.37\text{V}$, $E^\circ (\text{Ag}^+/\text{Ag}) = 0.8\text{ V}$.
- Q.36 The standard reduction potential at 25°C for the reduction of water
 $2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{OH}^-$ is -0.8277 volt . Calculate the equilibrium constant for the reaction
 $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ at 25°C .
- Q.37 At 25°C the value of K for the equilibrium $\text{Fe}^{3+} + \text{Ag} \rightleftharpoons \text{Fe}^{2+} + \text{Ag}^+$ is 0.531 mol/litre . The standard electrode potential for $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$ is 0.799V . What is the standard potential for $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$?
- Q.38 The EMF of the cell $\text{M} \mid \text{M}^{n+} (0.02\text{M}) \parallel \text{H}^+ (1\text{M}) \mid \text{H}_2(\text{g}) (1\text{ atm}), \text{Pt}$ at 25°C is 0.81V . Calculate the valency of the metal if the standard oxidation of the metal is 0.76V .
- Q.39 Equinormal Solutions of two weak acids, $\text{HA} (\text{pK}_a = 3)$ and $\text{HB} (\text{pK}_a = 5)$ are each placed in contact with standard hydrogen electrode at 25°C . When a cell is constructed by interconnecting them through a salt bridge, find the emf of the cell.
- Q.40 In two vessels each containing 500ml water, 0.5m mol of aniline ($K_b = 10^{-9}$) and 25mmol of HCl are added separately. Two hydrogen electrodes are constructed using these solutions. Calculate the emf of cell made by connecting them appropriately.
- Q.41 Calculate E° and E for the cell $\text{Sn} \mid \text{Sn}^{2+} (1\text{M}) \parallel \text{Pb}^{2+} \mid \text{Pb} (10^{-3}\text{M})$, $E^\circ (\text{Sn}^{2+} \mid \text{Sn}) = -0.14\text{V}$, $E^\circ (\text{Pb}^{2+} \mid \text{Pb}) = -0.13\text{V}$. Is cell representation is correct?
- Q.42 At what concentration of Cu^{2+} in a solution of CuSO_4 will the electrode potential be zero at 25°C ?
 Given : $E^\circ (\text{Cu} \mid \text{Cu}^{2+}) = -0.34\text{ V}$.
- Q.43 A zinc electrode is placed in a 0.1M solution at 25°C . Assuming that the salt is 20% dissociated at this dilutions calculate the electrode potential. $E^\circ (\text{Zn}^{2+} \mid \text{Zn}) = -0.76\text{V}$.
- Q.44 From the standard potentials shown in the following diagram, calculate the potentials E_1° and E_2° .



- Q.45 For the reaction, $4\text{Al(s)} + 3\text{O}_2(\text{g}) + 6\text{H}_2\text{O} + 40\text{H}^- \rightleftharpoons 4 [\text{Al}(\text{OH})_4^-]$; $E_{\text{cell}}^\circ = 2.73\text{ V}$. If $\Delta G_f^\circ (\text{OH}^-) = -157\text{ kJ mol}^{-1}$ and $\Delta G_f^\circ (\text{H}_2\text{O}) = -237.2\text{ kJ mol}^{-1}$, determine $\Delta G_f^\circ [\text{Al}(\text{OH})_4^-]$.

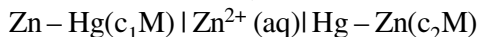
Concentration cells :

Q.46 Calculate the EMF of the following cell



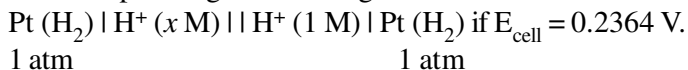
at 298 K.

Q.47 Calculate the EMF of the cell,

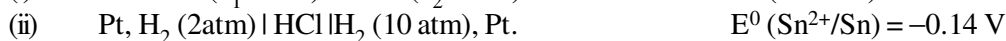
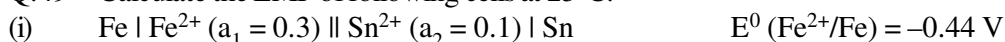


at 25°C, if the concentrations of the zinc amalgam are: $c_1 = 10\text{g}$ per 100g of mercury and $c_2 = 1\text{g}$ per 100 g of mercury.

Q.48 Calculate pH using the following cell :



Q.49 Calculate the EMF of following cells at 25°C.



Q.50 EMF of the cell $\text{Zn} | \text{ZnSO}_4 (a_1 = 0.2) || \text{ZnSO}_4 (a_2) | \text{Zn}$ is -0.0088V at 25°C . Calculate the value of a_2 .

CONDUCTANCE

Conductivities and cell constant:

Q.51 The resistance of a conductivity cell filled with 0.01N solution of NaCl is 210 ohm at 18°C . Calculate the equivalent conductivity of the solution. The cell constant of the conductivity cell is 0.88 cm^{-1} .

Q.52 The molar conductivity of 0.1 M CH_3COOH solution is $4.6 \text{ S cm}^2 \text{ mole}^{-1}$. What is the specific conductivity and resistivity of the solution ?

Q.53 The conductivity of pure water in a conductivity cell with electrodes of cross sectional area 4 cm^2 and 2 cm apart is $8 \times 10^{-7} \text{ S cm}^{-1}$.

(i) What is resistance of conductivity cell ?

(ii) What current would flow through the cell under an applied potential difference of 1 volt?

Q.54 Resistivity of 0.1M KCl solution is 213 ohm cm in a conductivity cell. Calculate the cell constant if its resistance is 330 ohm.

Q.55 Resistance of a 0.1M KCl solution in a conductance cell is 300 ohm and specific conductance of 0.1M KCl is $1.29 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$. The resistance of 0.1M NaCl solution in the same cell is 380 ohm. Calculate the equivalent conductance of the 0.1M NaCl solution.

Q.56 For 0.01N KCl, the resistivity 709.22 mho cm. Calculate the conductivity and equivalent conductance.

Q.57 A solution containing 2.08 g of anhydrous barium chloride in 400 CC of water has a specific conductivity $0.0058 \text{ ohm}^{-1}\text{cm}^{-1}$. What are molar and equivalent conductivities of this solution.

Application of Kohlrausch's law:

- Q.58 Equivalent conductance of 0.01 N Na_2SO_4 solution is $112.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$. The equivalent conductance at infinite dilution is $129.9 \text{ ohm}^{-1} \text{ cm}^2$. What is the degree of dissociation in 0.01 N Na_2SO_4 solution?
- Q.59 Specific conductance of a saturated solution of AgBr is $8.486 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C . Specific conductance of pure water at 25°C is $0.75 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-2}$. Λ_m^∞ for KBr, AgNO_3 and KNO_3 are 137.4, 133, 131 ($\text{S cm}^2 \text{ mol}^{-1}$) respectively. Calculate the solubility of AgBr in gm/litre.
- Q.60 Saturated solution of AgCl at 25°C has specific conductance of $1.12 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. The $\lambda_\infty \text{Ag}^+$ and $\lambda_\infty \text{Cl}^-$ are 54.3 and $65.5 \text{ ohm}^{-1} \text{ cm}^2 / \text{equi.}$ respectively. Calculate the solubility product of AgCl at 25°C .
- Q.61 Hydrofluoric acid is weak acid. At 25°C , the molar conductivity of 0.002M HF is $176.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$. If its $\Lambda_m^\infty = 405.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$, calculate its degree of dissociation and equilibrium constant at the given concentration.
- Q.62 The value of Λ_m^∞ for HCl, NaCl and $\text{CH}_3\text{CO}_2\text{Na}$ are 426.1, 126.5 and $91 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. Calculate the value of Λ_m^∞ for acetic acid. If the equivalent conductivity of the given acetic acid is 48.15 at 25°C , calculate its degree of dissociation.
- Q.63 Calculate the specific conductance of a 0.1 M aqueous solution of NaCl at room temperature, given that the mobilities of Na^+ and Cl^- ions at this temperature are 4.26×10^{-8} and $6.80 \times 10^{-8} \text{ m}^2 \text{ v}^{-1} \text{ s}^{-1}$, respectively.
- Q.64 For the strong electrolytes NaOH, NaCl and BaCl_2 the molar ionic conductivities at infinite dilution are 248.1×10^{-4} , 126.5×10^{-4} and $280.0 \times 10^{-4} \text{ mho cm}^2 \text{ mol}^{-1}$ respectively. Calculate the molar conductivity of Ba(OH)_2 at infinite dilution.
- Q.65 At 25°C , $\lambda_\infty(\text{H}^+) = 3.4982 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$ and $\lambda_\infty(\text{OH}^-) = 1.98 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$. Given: Sp. conductance = $5.1 \times 10^{-6} \text{ S m}^{-1}$ for H_2O , determine pH and K_w .

PROFICIENCY TEST

1. In highly alkaline medium, the anodic process during the electrolytic process is
$$4\text{OH}^- \longrightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-.$$
2. Compounds of active metals (Zn, Na, Mg) are reducible by H_2 whereas those of noble metals (Cu, Ag, Au) are not reducible.
3. The mass of a substance deposited on the cathode or anode during electrolysis is given by $w = \frac{EIt}{F}$.
4. Faraday's second law of electrolysis is related to the equivalent, mass of the electrolyte.
5. Equivalent conductance at infinite dilution of salt AB is equal to the sum of equivalent conductances of ions, A^+ and B^- at infinite dilution.
6. The standard reduction potential of $\text{Cl}^-|\text{AgCl}|\text{Ag}$ half-cell is related to that of $\text{Ag}^+|\text{Ag}$ half-cell through the expression $E_{\text{Ag}^+|\text{Ag}}^\circ = E_{\text{Cl}^-|\text{AgCl}|\text{Ag}}^\circ + \frac{RT}{F} \ln K_{\text{sp}}(\text{AgCl})$.
7. The cell potential is given by $E_{\text{cell}} = E_{\text{RP}(\text{cathode})} - E_{\text{RP}(\text{anode})}$.
8. A half-cell reaction is $\text{A}^{(x+n)} + n\text{e}^- \longrightarrow \text{A}^{x+}$. It is possible to determine the value of n from the measurements of cell potential.
9. In a galvanic cell, the half-cell with higher reduction potential acts as a reducing agent.
10. In an electrode concentration cell, the cell reaction $\text{Zn}(\text{c}_1) \longrightarrow \text{Zn}(\text{c}_2)$ will be spontaneous if $\text{c}_1 > \text{c}_2$.
11. The absolute value of electrode potential cannot be determined.
12. All chemical reactions used in galvanic cells are redox reactions.
13. The amount of the product formed by the passage of 1 coulomb of electricity through electrolyte is called electrochemical equivalent of the substance.
14. The redox reaction involved in galvanic cell is a non-spontaneous process.
15. In galvanic cell, the cathode is a –ve terminal of the cell.
16. The specific conductance of a 0.1 N KCl solution at 23°C is $0.012 \text{ ohm}^{-1} \text{ cm}^{-1}$. The resistance of the cell containing the solution at the same temperature was found to be 55 ohms. The cell constant is ____.
17. Dilute sulphuric acid on electrolysis liberates _____ at the anode.
18. The electrical conductivity of a solution of acetic acid will _____ if a solution of sodium hydroxide is added.
19. A cation having a _____ reduction potential is preferentially reduced at the cathode.

20. When an aqueous solution of sodium sulphate is electrolysed, the gases liberated at the anode & cathode are _____ and _____, respectively.
21. A cell in which two electrodes of the same metal are dipped in solutions of metal ion of different concentrations is called _____.
22. The half-cell involving the reaction,

$$\text{Cr}_2\text{O}_7^{2-}(\text{aq.}) + 14\text{H}^+(\text{aq.}) + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+}(\text{aq.}) + 7\text{H}_2\text{O}$$
 is represented as _____.
23. During discharge of lead storage battery, the overall reaction is _____.
24. In the calomel half-cell, the reduction reaction is _____.
25. Temperature coefficient and change in enthalpy are related by the expression _____.
26. In salt bridge, the electrolyte used should be _____.
27. In electrochemical cell, the electrical neutrality in two half cells is maintained by _____.
28. The E° value for $\text{H}_2 \longrightarrow 2\text{H}^+ + 2\text{e}^-$ is _____.
29. E°_{cell} of $E^\circ_{\text{oxi.}}(\text{anode}) +$ _____.
30. Coulomb refers to _____ of electricity while ampere refers to _____ at which it flows.
31. The cathodic reactions always involve _____.
32. During electrolysis of aqueous solution of CuSO_4 using Pt electrodes the product at anode is _____.
33. The quantity of electricity required for complete reduction of 0.5 mole MnO_4^- to Mn^{2+} is _____ C.
34. During electrolysis process _____ energy is converted into _____.
35. $\wedge_{\text{eq}} \times \text{normality} =$ _____.

MIDDLE GAME

- Q.1 Same quantity of electricity is being used to liberate iodine (at anode) and a metal x (at cathode). The mass of x deposited is 0.617g and the iodine is completely reduced by 46.3 cc of 0.124M sodium thiosulphate. Find the equivalent mass of x.
- Q.2 The standard reduction potential values, $E^0(\text{Bi}^{3+}|\text{Bi})$ and $E^0(\text{Cu}^{2+}|\text{Cu})$ are 0.226V and 0.344V respectively. A mixture of salts of bismuth and copper at unit concentration each is electrolysed at 25°C. to what value can $[\text{Cu}^{2+}]$ be brought down before bismuth starts to deposit, in electrolysis.
- Q.3 In a fuel cell, H_2 & O_2 react to produce electricity. In the process, H_2 gas is oxidized at the anode & O_2 at the cathode. If 67.2 litre of H_2 at STP react in 15 minutes, what is the average current produced? If the entire current is used for electrode deposition of Cu from Cu (II) solution, how many grams of Cu will be deposited?
- Anode : $\text{H}_2 + 2\text{OH}^- \longrightarrow 2\text{H}_2\text{O} + 2\text{e}^-$ Cathode : $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \longrightarrow 4\text{OH}^-$
- Q.4 One of the methods of preparation of per disulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$, involve electrolytic oxidation of H_2SO_4 at anode ($2\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{S}_2\text{O}_8 + 2\text{H}^+ + 2\text{e}^-$) with oxygen and hydrogen as by-products. In such an electrolysis, 9.722 L of H_2 and 2.35 L of O_2 were generated at STP. What is the weight of $\text{H}_2\text{S}_2\text{O}_8$ formed?
- Q.5 During the discharge of a lead storage battery the density of sulphuric acid fell from 1.294 to 1.139 g.mL⁻¹. H_2SO_4 of density 1.294 g mL⁻¹ is 39% and that of density 1.39 g mL⁻¹ is 20% by weight. The battery holds 3.5L of acid and the volume practically remains constant during the discharge. Calculate the number of ampere hours for which the battery must have been used. The discharging reactions are:
- $\text{Pb} + \text{SO}_4^{2-} \rightleftharpoons \text{PbSO}_4 + 2\text{e}^-$ (anode)
- $\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \rightleftharpoons \text{PbSO}_4 + 2\text{H}_2\text{O}$ (cathode)
- Q.6 The emf of the cells obtained by combining Zn and Cu electrode of a Daniel cell with N calomel electrode in two different arrangements are 1.083V and 0.018V respectively at 25°C. If the standard reduction potential of N calomel electrode is -0.28V and that of Zn is -0.76 V, find the emf of Daniel cell.
- Q.7 Given the standard reduction potentials $\text{TI}^+ + \text{e}^- \rightleftharpoons \text{TI}$, $E^0 = -0.34\text{V}$ and $\text{TI}^{3+} + 2\text{e}^- \rightleftharpoons \text{TI}^+$, $E^0 = 1.25\text{V}$. Examine the spontaneity of the reaction, $3\text{TI}^+ \rightleftharpoons 2\text{TI} + \text{TI}^{3+}$. Also find E^0 for this disproportionation.
- Q.8 The emf of the cell $\text{Ag}|\text{AgI}|\text{KI}(0.05\text{M})||\text{AgNO}_3(0.05\text{M})|\text{Ag}$ is 0.788V. Calculate the solubility product of AgI.
- Q.9 The cell $\text{Pt}, \text{H}_2(1 \text{ atm})|\text{H}^+(\text{pH}=x)||\text{Normal calomel Electrode}$ has an EMF of 0.67V at 25°C. Calculate the pH of the solution. The oxidation potential of the calomel electrode on hydrogen scale is -0.28 V.
- Q.10 Estimate the cell potential of a Daniel cell having 1 M Zn^{++} & originally having 1 M Cu^{++} after sufficient NH_3 has been added to the cathode compartment to make NH_3 concentration 2 M.
- K_f for $[\text{Cu}(\text{NH}_3)_4]^{2+} = 1 \times 10^{12}$, E^0 for the reaction,
 $\text{Zn} + \text{Cu}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Cu}$ is 1.1 V.
- Q.11 Consider the cell $\text{Ag}|\text{AgBr(s)}|\text{Br}^-||\text{AgCl(s)}, \text{Ag}|\text{Cl}^-$ at 25°C. The solubility product constants of AgBr & AgCl are respectively 5×10^{-13} & 1×10^{-10} . For what ratio of the concentrations of Br^- & Cl^- ions would the emf of the cell be zero?
- Q.12 The pK_{sp} of AgI is 16.07. If the E^0 value for $\text{Ag}^+|\text{Ag}$ is 0.7991 V. Find the E^0 for the half cell reaction $\text{AgI(s)} + \text{e}^- \rightleftharpoons \text{Ag} + \text{I}^-$.

- Q.13 Voltage of the cell $\text{Pt}, \text{H}_2 (1 \text{ atm}) | \text{HOCN} (1.3 \times 10^{-3} \text{ M}) || \text{Ag}^+ (0.8 \text{ M}) | \text{Ag(s)}$ is 0.982 V. Calculate the K_a for HOCN. Neglect $[\text{H}^+]$ because of oxidation of $\text{H}_2(\text{g})$.
 $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag(s)} = 0.8 \text{ V}$.
- Q.14 The normal potential of Zn referred to SHE is 0.76V and that of Cu is -0.34V at 25°C . When excess of Zn is added to CuSO_4 , Zn displaces Cu^{2+} till equilibrium is reached. What is the ratio of Zn^{2+} to Cu^{2+} ions at equilibrium?
- Q.15 Calculate the potential of an indicator electrode versus the standard hydrogen electrode, which originally contained 0.1M MnO_4^- and 0.8M H^+ and which was treated with 90% of the Fe^{2+} necessary to reduce all the MnO_4^- to Mn^{2+} .
 $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}, E^0 = 1.51\text{V}$
- Q.16 K_d for complete dissociation of $[\text{Ag}(\text{NH}_3)_2]^+$ into Ag^+ and 2NH_3 is 6×10^{-8} . Calculate E^0 for the following half reaction; $\text{Ag}(\text{NH}_3)_2^+ + \text{e}^- \rightleftharpoons \text{Ag} + 2\text{NH}_3$
 $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}, E^0 = 0.799 \text{ V}$
- Q.17 The overall formation constant for the reaction of 6 mol of CN^- with cobalt (II) is 1×10^{19} . The standard reduction potential for the reaction $[\text{Co}(\text{CN})_6]^{3-} + \text{e}^- \rightleftharpoons [\text{Co}(\text{CN})_6]^{4-}$ is -0.83 V . Calculate the formation constant of $[\text{Co}(\text{CN})_6]^{3-}$.
 Given $\text{Co}^{3+} + \text{e}^- \rightleftharpoons \text{Co}^{2+}; E^0 = 1.82 \text{ V}$
- Q.18 Calculate the emf of the cell
 $\text{Pt}, \text{H}_2(1.0 \text{ atm}) | \text{CH}_3\text{COOH} (0.1\text{M}) || \text{NH}_3(\text{aq}, 0.01\text{M}) | \text{H}_2 (1.0 \text{ atm}),$
 $\text{Pt } K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}, K_b(\text{NH}_3) = 1.8 \times 10^{-5}.$
- Q.19 A current of 3 amp was passed for 2 hour through a solution of CuSO_4 , 3 g of Cu^{2+} ions were deposited as Cu at cathode. Calculate percentage current efficiency of the process.
- Q.20 The Edison storage cell is represented as $\text{Fe(s)} | \text{FeO(s)} | \text{KOH(aq)} | \text{Ni}_2\text{O}_3(\text{s}) | \text{Ni(s)}$ The half-cell reaction are
 $\text{Ni}_2\text{O}_3(\text{s}) + \text{H}_2\text{O(l)} + 2\text{e}^- \rightleftharpoons 2\text{NiO(s)} + 2\text{OH}^-, E^0 = +0.40\text{V}$
 $\text{FeO(s)} + \text{H}_2\text{O(l)} + 2\text{e}^- \rightleftharpoons \text{Fe(s)} + 2\text{OH}^-, E^0 = -0.87\text{V}$
- (i) What is the cell reaction?
 (ii) What is the cell e.m.f.? How does it depend on the concentration of KOH?
 (iii) What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3 ?
- Q.21 For the galvanic cell : $\text{Ag} | \text{AgCl(s)} | \text{KCl} (0.2\text{M}) || \text{KBr} (0.001 \text{ M}) | \text{AgBr(s)} | \text{Ag},$
 Calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25°C .
 $[K_{\text{sp}}(\text{AgCl}) = 2.8 \times 10^{-10}; K_{\text{sp}}(\text{AgBr}) = 3.3 \times 10^{-13}]$
- Q.22 An aqueous solution of NaCl on electrolysis gives $\text{H}_{2(\text{g})}$, $\text{Cl}_{2(\text{g})}$ and NaOH according to the reaction:
 $2\text{Cl}^-_{(\text{aq})} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{OH}^-_{(\text{aq})} + \text{H}_{2(\text{g})} + \text{Cl}_{2(\text{g})}$
 A direct current of 25 amperes with a current efficiency of 62% is passed through 20 liters of NaCl solution (20% by weight). Write down the reactions taking place at the anode and the cathode. How long will it take to produce 1 Kg of Cl_2 ? What will be the molarity of the solution with respect to hydroxide ion? (Assume no loss due to evaporation).
- Q.23 An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolyzed until all the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 ml and the current at 1.2 amp. Calculate the volume of gases evolved at NTP during the entire electrolysis.

- Q.24 In the refining of silver by electrolytic method what will be the weight of 100 gm Ag anode if 5 ampere current is passed for 2 hours? Purity of silver is 95% by weight.
- Q.25 Hydrogen peroxide can be prepared by successive reactions:
 $2\text{NH}_4\text{HSO}_4 \rightarrow \text{H}_2 + (\text{NH}_4)_2\text{S}_2\text{O}_8$
 $(\text{NH}_4)_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_4\text{HSO}_4 + \text{H}_2\text{O}_2$
 The first reaction is an electrolytic reaction the second is steam distillation. What amount of current would have to be used in first reaction to produce enough intermediate to yield 100 gm pure H_2O_2 per hour? Assume 50% anode current efficiency.
- Q.26 Dal lake has water 8.2×10^{12} litre approximately. A power reactor produces electricity at the rate of 1.5×10^6 coulomb per second at an appropriate voltage. How many years would it take to electrolyse the lake?
- Q.27 Calculate the potential at 25°C for the cell
 $\text{Cd} | \text{Cd}^{2+} (2.00 \text{ M}) || \text{Pb}^{2+} (0.0010 \text{ M}) | \text{Pb}$
 Given $E^\circ_{\text{cell}} = 0.277 \text{ V}$.
- Q.28 Calculate E° for the following reactions at 298 K,
 $\text{Ag}(\text{NH}_3)_2^+ + e^- \rightleftharpoons \text{Ag} + 2\text{NH}_3$
 $\text{Ag}(\text{CN})_2^- + e^- \rightleftharpoons \text{Ag} + 2\text{CN}^-$
 Given: $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.7991 \text{ V}$, $K_{\text{Ins}}[\text{Ag}(\text{NH}_3)_2^+] = 6.02 \times 10^{-8}$ and $K_{\text{Ins}}[\text{Ag}(\text{CN})_2^-] = 1.995 \times 10^{-19}$
- Q.29 Determine the degree of hydrolysis and hydrolysis constant of aniline hydrochloride in M/32 solution of salt at 298 K from the following cell data at 298 K.
 $\text{Pt} | \text{H}_2 (1 \text{ atm}) | \text{H}^+ (1 \text{ M}) || \text{M/32 C}_6\text{H}_5\text{NH}_3\text{Cl} | \text{H}_2 (1 \text{ atm}) | \text{Pt}$; $E_{\text{cell}} = -0.188 \text{ V}$.
- Q.30 The emf of the cell, $\text{Pt} | \text{H}_2 (1 \text{ atm}), | \text{H}^+ (0.1 \text{ M}, 30 \text{ ml}) || \text{Ag}^+ (0.8 \text{ M}) | \text{Ag}$ is 0.9 V. Calculate the emf when 40 ml of 0.05 M NaOH is added.
- Q.31 Given, $E^\circ = -0.268 \text{ V}$ for the $\text{Cl}^- | \text{PbCl}_2 | \text{Pb}$ couple and -0.126 V for the $\text{Pb}^{2+} | \text{Pb}$ couple, determine K_{sp} for PbCl_2 at 25°C ?
- Q.32 The equivalent conductance of 0.10 N solution of MgCl_2 is $97.1 \text{ mho cm}^2 \text{ eq}^{-1}$ at 25°C . a cell with electrode that are 1.5 cm^2 in surface area and 0.5 cm apart is filled with 0.1 N MgCl_2 solution. How much current will flow when potential difference between the electrodes is 5 volt.
- Q.33 A dilute aqueous solution of KCl was placed between two electrodes 10 cm apart, across which a potential of 6 volt was applied. How far would the K^+ ion move in 2 hours at 25°C ? Ionic conductance of K^+ ion at infinite dilution at 25°C is $73.52 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$?
- Q.34 When a solution of specific conductance $1.342 \text{ ohm}^{-1} \text{ metre}^{-1}$ was placed in a conductivity cell with parallel electrodes, the resistance was found to be 170.5 ohm. Area of electrodes is $1.86 \times 10^{-4} \text{ m}^2$. Calculate separation of electrodes.
- Q.35 The specific conductance at 25°C of a saturated solution of SrSO_4 is $1.482 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ while that of water used is $1.5 \times 10^{-6} \text{ mho cm}^{-1}$. Determine at 25°C the solubility in gm per litre of SrSO_4 in water. Molar ionic conductance of Sr^{2+} and SO_4^{2-} ions at infinite dilution are 59.46 and $79.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ respectively. [Sr = 87.6 , S = 32 , O = 16]

ZENITH

- Q.1 A lead storage cell is discharged which causes the H_2SO_4 electrolyte to change from a concentration of 34.6 % by weight (density 1.261 g mL^{-1} at 25°C) to 27 % by weight. The original volume of electrolyte is one litre. Calculate the total charge released at anode of the battery. Note that the water is produced by the cell reaction as H_2SO_4 is used up. Over all reaction is
- $$\text{Pb(s)} + \text{PbO}_2\text{(s)} + 2\text{H}_2\text{SO}_4\text{(l)} \longrightarrow 2\text{PbSO}_4\text{(s)} + 2\text{H}_2\text{O(l)}$$
- Q.2 Assume that impure copper contains only iron, silver and a gold as impurities. After passage of 140 A, for 482.5s of the mass of the anode decreased by 22.260g and the cathode increased in mass by 22.011 g. Estimate the % iron and % copper originally present.
- Q.3 100ml $\text{CuSO}_4\text{(aq)}$ was electrolyzed using inert electrodes by passing 0.965 A till the pH of the resulting solution was 1. The solution after electrolysis was neutralized, treated with excess KI and titrated with 0.04M $\text{Na}_2\text{S}_2\text{O}_3$. Volume of $\text{Na}_2\text{S}_2\text{O}_3$ required was 35 ml. Assuming no volume change during electrolysis, calculate:
- (a) duration of electrolysis if current efficiency is 80% (b) initial concentration (M) of CuSO_4 .
- Q.4 Calculate the equilibrium constant for the reaction:
- $$3\text{Sn(s)} + 2\text{Cr}_2\text{O}_7^{2-} + 28\text{H}^+ \longrightarrow 3\text{Sn}^{4+} + 4\text{Cr}^{3+} + 14\text{H}_2\text{O}$$
- E^0 for $\text{Sn}/\text{Sn}^{2+} = 0.136 \text{ V}$ E^0 for $\text{Sn}^{2+}/\text{Sn}^{4+} = -0.154 \text{ V}$
 E^0 for $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+} = 1.33 \text{ V}$
- Q.5 Calculate the equilibrium concentrations of all ions in an ideal solution prepared by mixing 25.00 mL of 0.100M Ti^+ with 25.00mL of 0.200M Co^{3+} .
- $E^0 (\text{Ti}^+/\text{Ti}^{3+}) = -1.25 \text{ V}$; $E^0 (\text{Co}^{3+}/\text{Co}^{2+}) = 1.84 \text{ V}$
- Q.6 Calculate the voltage, E, of the cell at 25°C
- $$\text{Mn(s)} \mid \text{Mn(OH)}_2\text{(s)} \mid \text{Mn}^{2+}(\text{x M}), \text{OH}^-(1.00 \times 10^{-4}\text{M}) \parallel \text{Cu}^{2+}(0.675\text{M}) \mid \text{Cu(s)}$$
- given that $K_{\text{sp}} = 1.9 \times 10^{-13}$ for $\text{Mn(OH)}_2\text{(s)}$ $E^0 (\text{Mn}^{2+}/\text{Mn}) = -1.18 \text{ V}$
- Q.7 Calculate the voltage, E, of the cell
- $$\text{Ag(s)} \mid \text{AgIO}_3\text{(s)} \mid \text{Ag}^+(\text{x M}), \text{HIO}_3(0.300\text{M}) \parallel \text{Zn}^{2+}(0.175\text{M}) \mid \text{Zn(s)}$$
- if $K_{\text{sp}} = 3.02 \times 10^{-8}$ for $\text{AgIO}_3\text{(s)}$ and $K_{\text{a}} = 0.162$ for HIO_3 .
- Q.8 The voltage of the cell
- $$\text{Pb(s)} \mid \text{PbSO}_4\text{(s)} \mid \text{NaHSO}_4(0.600\text{M}) \parallel \text{Pb}^{2+}(2.50 \times 10^{-5}\text{M}) \mid \text{Pb(s)}$$
- is $E = +0.061 \text{ V}$. Calculate $K_2 = [\text{H}^+][\text{SO}_4^{2-}]/[\text{HSO}_4^-]$, the dissociation constant for HSO_4^- .
Given : $\text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \rightleftharpoons \text{PbSO}_4\text{(s)} + 2\text{e}^-$ ($E^0 = 0.356$) $E^0(\text{Pb}^{2+}/\text{Pb}) = -0.126 \text{ V}$
- Q.9 The voltage of the cell
- $$\text{Zn(s)} \mid \text{Zn(CN)}_4^{2-}(0.450\text{M}), \text{CN}^-(2.65 \times 10^{-3}\text{M}) \parallel \text{Zn}^{2+}(3.84 \times 10^{-4}\text{M}) \mid \text{Zn(s)}$$
- is $E = +0.099 \text{ V}$. Calculate the constant K_f for $\text{Zn}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Zn(CN)}_4^{2-}$, the only $\text{Zn}^{2+} + \text{CN}^-$ complexation reaction of importance.
- Q.10 An external current source giving a current of 5.0 A was joined with Daniel cell and removed after 10 hrs. Before passing the current the LHE and RHE contained 1L each of 1M Zn^{2+} and Cu^{2+} respectively. Find the EMF supplied by the Daniel cell after removal of the external current source. E^0 of Zn^{2+}/Zn and Cu^{2+}/Cu at 25°C is -0.76 and $+0.34\text{V}$ respectively.

- Q.11 Determine at 298 for cell
 $\text{Pt} | \text{Q}, \text{QH}_2, \text{H}^+ || 1\text{M KCl} | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg}(\text{l}) | \text{Pt}$
- (a) it's emf when $\text{pH} = 5.0$
 (b) the pH when $E_{\text{cell}} = 0$
 (c) the positive electrode when $\text{pH} = 7.5$
 given $E_{\text{RP(RHS)}}^0 = 0.28$, $E_{\text{RP(LHS)}}^0 = 0.699$
- Q.12 At 25°C , $\Delta H_f(\text{H}_2\text{O}, \text{l}) = -56700 \text{ cal/mol}$ and energy of ionization of $\text{H}_2\text{O}(\text{l}) = 19050 \text{ cal/mol}$. What will be the reversible EMF at 25°C of the cell,
 $\text{Pt} | \text{H}_2(\text{g}) (1 \text{ atm}) | \text{H}^+ || \text{OH}^- | \text{O}_2(\text{g}) (1 \text{ atm}) | \text{Pt}$, if at 26°C the emf increases by 0.001158 V .
- Q.13 Calculate the cell potential of a cell having reaction: $\text{Ag}_2\text{S} + 2\text{e}^- \rightleftharpoons 2\text{Ag} + \text{S}^{2-}$ in a solution buffered at $\text{pH} = 3$ and which is also saturated with $0.1 \text{ M H}_2\text{S}$.
 For H_2S : $K_1 = 10^{-8}$ and $K_2 = 1.1 \times 10^{-13}$, $K_{\text{sp}}(\text{Ag}_2\text{S}) = 2 \times 10^{-49}$, $E_{\text{Ag}^+/\text{Ag}}^\circ = 0.8$.
- Q.14 Calculate the solubility and solubility product of $\text{Co}_2[\text{Fe}(\text{CN})_6]$ in water at 25°C from the following data:
 Conductivity of a saturated solution of $\text{Co}_2[\text{Fe}(\text{CN})_6]$ is $2.06 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ and that of water used $4.1 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$. The ionic molar conductivities of Co^{2+} and $\text{Fe}(\text{CN})_6^{4-}$ are $86.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and $444.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.
- Q.15 A sample of water from a large swimming pool has a resistance of 9200Ω at 25°C when placed in a certain conductance cell. When filled with 0.02 M KCl solution, the cell has a resistance of 85Ω at 25°C . 500 gm of NaCl were dissolved in the pool, which was thoroughly stirred. A sample of this solution gave a resistance of 7600Ω . Calculate the volume of water in the pool.
 Given : Molar conductance of NaCl at that concentration is $126.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and molar conductivity of KCl at 0.02 M is $138 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

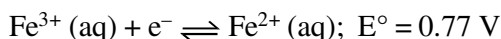
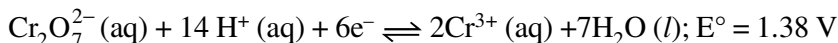
SUHANNA SAFAR

OBJECTIVE

- Q.1 A dilute aqueous solution of Na_2SO_4 is electrolysed using platinum electrodes. The products at the anode and cathode are
(A) O_2, H_2 (B) $\text{S}_2\text{O}_8^{2-}, \text{Na}$ (C) O_2, Na (D) $\text{S}_2\text{O}_8^{2-}, \text{H}_2$ [JEE 1996]
- Q.2 The standard reduction potentials of Cu^{2+}/Cu and $\text{Cu}^{2+}/\text{Cu}^+$ are 0.337 and 0.153 V respectively. The standard electrode potential of Cu^+/Cu half cell is
(A) 0.184 V (B) 0.827 V (C) 0.521 V (D) 0.490 V [JEE 1997]
- Q.3 A standard hydrogen electrode has zero electrode potential because
(A) hydrogen is easier to oxidise
(B) this electrode potential is assumed to be zero
(C) hydrogen atom has only one electron
(D) hydrogen is the lightest element. [JEE 1997]
- Q.4 The standard reduction potential values of the three metallic cations X, Y, Z are 0.52, -3.03, and -1.18 V respectively. The order of reducing power of the corresponding metals is
(A) $\text{Y} > \text{Z} > \text{X}$ (B) $\text{X} > \text{Y} > \text{Z}$ (C) $\text{Z} > \text{Y} > \text{X}$ (D) $\text{Z} > \text{X} > \text{Y}$ [JEE 1998]
- Q.5 A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y^- and 1 M 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 X
(C) Y will oxidise both X and Z (D) Y will reduce both X and Z. [JEE 1999]
- Q.6 For the electrochemical cell, $\text{M} | \text{M}^+ || \text{X}^- | \text{X}$, $E^\circ (\text{M}^+/\text{M}) = 0.44 \text{ V}$ and $E^\circ (\text{X}/\text{X}^-) = 0.33 \text{ V}$. From this data, one can deduce that
(A) $\text{M} + \text{X} \longrightarrow \text{M}^+ + \text{X}^-$ is the spontaneous reaction
(B) $\text{M}^+ + \text{X}^- \longrightarrow \text{M} + \text{X}$ is the spontaneous reaction
(C) $E_{\text{cell}} = 0.77 \text{ V}$
(D) $E_{\text{cell}} = -0.77 \text{ V}$ [JEE 2000]
- Q.7 The reaction,
$$3\text{ClO}^-(\text{aq}) \longrightarrow \text{ClO}_3^-(\text{aq}) + 2\text{Cl}^-(\text{aq})$$

is an example of
(A) Oxidation reaction (B) Reduction reaction
(C) Disproportionation reaction (D) Decomposition reaction [JEE 2001]
- Q.8 The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is
(A) $\text{LiCl} > \text{NaCl} > \text{KCl}$ (B) $\text{KCl} > \text{NaCl} > \text{LiCl}$
(C) $\text{NaCl} > \text{KCl} > \text{LiCl}$ (D) $\text{LiCl} > \text{KCl} > \text{NaCl}$ [JEE 2001]
- Q.9 Saturated solution of KNO_3 is used to make salt bridge because
(A) velocity of K^+ is greater than that of NO_3^-
(B) velocity of NO_3^- is greater than that of K^+
(C) velocities of both K^+ and NO_3^- are nearly the same
(D) KNO_3 is highly soluble in water [JEE 2001]

- Q.10 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 quantitative estimation of aqueous $\text{Fe}(\text{NO}_3)_2$

(A) MnO_4^- can be used in aqueous HCl

(B) $\text{Cr}_2\text{O}_7^{2-}$ can be used in aqueous HCl

(C) MnO_4^- can be used in aqueous H_2SO_4

(D) $\text{Cr}_2\text{O}_7^{2-}$ can be used in aqueous H_2SO_4 [JEE 2002]

- Q.11 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.

[JEE 2003]

- Q.12 $\text{Zn} | \text{Zn}^{2+} (a = 0.1\text{M}) || \text{Fe}^{2+} (a = 0.01\text{M}) | \text{Fe}$. The emf of the above cell is 0.2905 V. Equilibrium constant for the cell reaction is

(A) $10^{0.32/0.0591}$

(B) $10^{0.32/0.0295}$

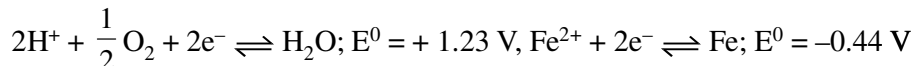
(C) $10^{0.26/0.0295}$

(D) $e^{0.32/0.295}$

[JEE 2004]

- Q.13 The half cell reactions for rusting of iron are:

[JEE 2005]



ΔG^0 (in kJ) for the reaction is:

(A) -76

(B) -322

(C) -122

(D) -176

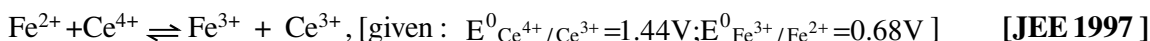
SUBJECTIVE

- Q.14 The standard reduction potential for $\text{Cu}^{2+} / \text{Cu}$ is 0.34 V. Calculate the reduction potential at pH = 14 for the above couple. K_{sp} of $\text{Cu}(\text{OH})_2$ is 1×10^{-19} . [JEE 1996]

- Q.15 Electrolysis of a solution of MnSO_4 in aqueous sulphuric acid is a method for the preparation of MnO_2 as per the reaction, $\text{Mn}^{2+}_{\text{aq}} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2(\text{s}) + 2\text{H}^+_{\text{aq}} + \text{H}_2(\text{g})$. Passing a current of 27 A for 24 hours gives one kg of MnO_2 . What is the value of current efficiency? Write the reaction taking place at the cathode and at the anode. [JEE 1997]

- Q.16 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^3 . [JEE 1997]

- Q.17 Calculate the equilibrium constant for the reaction



Q.18 Calculate the equilibrium constant for the reaction, $2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$. The standard reduction potentials in acidic conditions are 0.77 and 0.54 V respectively for $\text{Fe}^{3+}/\text{Fe}^{2+}$ and I_3^-/I^- couples. **[JEE 1998]**

Q.19 Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell $\text{Ag}|\text{Ag}^+(\text{satd. Ag}_2\text{CrO}_4 \text{ soln.})||\text{Ag}^+(0.1 \text{ M})|\text{Ag}$ is 0.164 V at 298K. **[JEE 1998]**

Q.20 Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 mintue. It was founf that agfter 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. **[JEE 2000]**

Q.21 The following electrochemical cell has been set up
 $\text{Pt}_{(\text{I})} | \text{Fe}^{3+}, \text{Fe}^{2+}(a=1) || \text{Ce}^{4+}, \text{Ce}^{3+}(a=1) | \text{Pt}_{(\text{II})}$

$$E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V and } E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.61 \text{ V}$$

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? **[JEE 2000]**

Q.22 The standard potential of the following cell is 0.23 V at 15°C & 0.21 V at 35°C
 $\text{Pt} | \text{H}_2(\text{g}) | \text{HCl}(\text{aq}) | \text{AgCl}(\text{s}) | \text{Ag}(\text{s})$

(i) Write the cell reaction.

(ii) Calculate $\Delta H^\circ, \Delta S^\circ$ 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 standard reduction potential of the Ag^+/Ag couple is 0.80 V at 25°C . **[JEE 2001]**

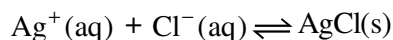
Q.23 Two students use same stock solution of ZnSO_4 and a solution of CuSO_4 . The e.m.f of one cell is 0.3 V higher than the other. The conc. of CuSO_4 in the cell with higher e.m.f value is 0.5 M. Find out the conc. of CuSO_4 in the other cell $\left(\frac{2.303 RT}{F} = 0.06 \right)$. **[JEE 2003]**

Q.24 Find the equilibrium constant at 298 K for the reaction,
 $\text{Cu}^{2+}(\text{aq}) + \text{In}^{2+}(\text{aq}) \rightleftharpoons \text{Cu}^+(\text{aq}) + \text{In}^{3+}(\text{aq})$

$$\text{Given that } E^\circ_{\text{Cu}^{2+}|\text{Cu}^+} = 0.15 \text{ V}, E^\circ_{\text{In}^{3+}|\text{In}^{2+}} = -0.42 \text{ V}, E^\circ_{\text{In}^{2+}|\text{In}^+} = -0.40 \text{ V}$$

[JEE 2004]

Q.25(a) Calculate ΔG_f° of the following reaction



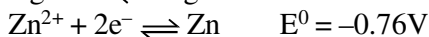
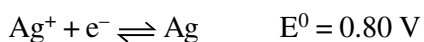
$$\text{Given: } \Delta G_f^\circ(\text{AgCl}) = -109 \text{ kJ/mole}, \Delta G_f^\circ(\text{Cl}^-) = -129 \text{ kJ/mole}, \Delta G_f^\circ(\text{Ag}^+) = 77 \text{ kJ/mole}$$

Represent the above reaction in form of a cell

Calculate E° of the cell. Find $\log_{10} K_{\text{SP}}$ of AgCl

(b) 6.593×10^{-2} g of metallic Zn (amu = 65.39) was added to 100 ml of saturated solution of AgCl .

$$\text{Calculate } \log_{10} \left[\frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} \right], \text{ given that}$$



Also find how many moles of Ag will be formed?

[JEE 2005]

ANSWER KEY
EASY RIDE

- Q.1 (a) 6.02×10^{22} electrons lost, (b) 1.89×10^{22} electrons gained, (c) (b) 1.80×10^{23} electrons gained
- Q.2 (a) 0.75 F, (b) 0.69 F, (c) 1.1 F
- Q.3 (i) 54 gm, (ii) 16.35 gm
- Q.4 1.023×10^5 sec
- Q.5 1.12 mol, 12.535 litre
- Q.6 0.112 litre
- Q.7 0.24 gms
- Q.8 Rs. 0.75x
- Q.9 (i) 2.1554 gm ; (ii) 1336. 15 sec
- Q.10 115800C, 347.4 kJ
- Q.11 $t = 193$ sec
- Q.12 $n = 4$
- Q.13 $\text{Cu}^{2+} = 0.08\text{M}$, $\text{H}^+ = 0.04\text{M}$, $\text{SO}_4^{2-} = 0.1\text{M}$
- Q.14 $A = 114$, $Q = 5926.8\text{C}$
- Q.15 Final weight = 9.6g, 0.01Eq of acid
- Q.16 (a) $V(\text{O}_2) = 6.2\text{L}$, (b) $V(\text{O}_2) = 0.824\text{L}$
- Q.17 $t = 93.65$ sec.
- Q.18 60 %
- Q.19 (i) 482.5 sec (ii) 0.3175 gm (iii) 0.327 gm
- Q.20 $7.958 \times 10^{-5}\text{M}$
- Q.21 1.825 g
- Q.22 2M
- Q.23 (a) $\text{Zn} | \text{Zn}^{2+} || \text{Cd}^{2+} | \text{Cd}$, (b) $\text{Pt}, \text{H}_2 | \text{H}^+ || \text{Ag}^+ | \text{Ag}$, (c) $\text{Cu} | \text{Cu}^{2+} || \text{Cl}^- | \text{Hg}_2\text{Cl}_2 | \text{Hg}$
(d) $\text{Pt} | \text{Fe}^{2+}, \text{Fe}^{3+} || \text{Cr}_2\text{O}_7^{2-}, \text{Cr}^{3+} | \text{Pt}$
- Q.24 (a) $2\text{Ag} + \text{Cu}^{2+} \longrightarrow 2\text{Ag}^+ + \text{Cu}$, (b) $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$
(c) $2\text{Cl}^- + 2\text{Ag}^+ \longrightarrow 2\text{Ag} + \text{Cl}_2$, (d) $\text{H}_2 + \text{Cd}^{2+} \longrightarrow \text{Cd} + 2\text{H}^+$
- Q.25
- | | |
|--|--|
| Anode | Cathode |
| (a) $\text{Zn} \text{Zn}^{2+}$ | $\text{H}^+, \text{H}_2 \text{Pt}$ |
| (b) $\text{Pt} \text{Sn}^{2+}, \text{Sn}^{4+}$ | $\text{Fe}^{3+}, \text{Fe}^{2+} \text{Pt}$ |
| (c) $\text{Pt} \text{Fe}^{2+}, \text{Fe}^{3+}$ | $\text{MnO}_4^-, \text{Mn}^{2+} \text{Pt}$ |
| (d) $\text{Pb} \text{Pb}^{2+}$ | $\text{Br}_2, \text{Br}^- \text{Pt}$] |
- Q.26 1.61 V
- Q.27 1.35 V
- Q.28 1.68 V
- Q.29 -0.80 V, NO
- Q.30 0.53 V, disproportionation
- Q.31 -0.0367 V
- Q.32 $E_{\text{cell}}^0 = -0.36$ V, not spontaneous
- Q.33 $E = 1.159\text{V}$
- Q.34 $K_c = 2.18 \times 10^{26}$
- Q.35 $K_c = 1.864 \times 10^{107}$, $\Delta G^0 = -611.8$ kJ
- Q.36 $K_w \approx 10^{-14}$
- Q.37 $E^0 = 0.7826$ V
- Q.38 $n = 2$
- Q.39 $E = 0.059$
- Q.40 $E = 0.395$ V
- Q.41 $E_{\text{cell}}^0 = +0.01\text{V}$, $E_{\text{cell}} = -0.0785\text{V}$, correct representation is $\text{Pb} | \text{Pb}^{2+} (10^{-3}\text{M}) || \text{Sn}^{2+} (1\text{M}) | \text{Sn}$
- Q.42 $[\text{Cu}^{2+}] = 2.97 \times 10^{-12}\text{M}$ for $E = 0$
- Q.43 $E = -0.81\text{eV}$
- Q.44 0.52 V, 0.61 V
- Q.45 -1.30×10^3 kJ mol⁻¹
- Q.46 0.0295 V
- Q.47 0.0295 V
- Q.48 pH = 4
- Q.49 (i) $E = 0.286\text{V}$; (ii) $E = -0.0206\text{V}$
- Q.50 $a_2 = 0.1006$ M
- Q.51 419 S cm² equivalent⁻¹
- Q.52 0.00046 S cm⁻¹; 2174 ohm cm
- Q.53 (i) 6.25×10^5 ohm, (ii) 1.6×10^{-6} amp
- Q.54 1.549 cm⁻¹
- Q.55 101.8 ohm⁻¹ cm² / gm equivalent
- Q.56 0.0141 mho g equiv⁻¹ m², 0.141 mho m⁻¹
- Q.57 (i) 232 Mho cm² mol⁻¹, (ii) 116 Mho cm² equivalent⁻¹
- Q.58 0.865
- Q.59 1.33×10^{-4} gm/litre
- Q.60 8.74×10^{-11} mole² /litre²
- Q.61 $\alpha = 0.435$, $k = 6.7 \times 10^{-4}$
- Q.62 (i) 390.6 S cm² mol⁻¹ (ii) 12.32%
- Q.63 1.067 S m⁻¹
- Q.64 523.2×10^{-4} mho cm² mol⁻¹
- Q.65 (i) 6.98 (ii) 1.08×10^{-14}

PROFICIENCY TEST

- | | | | | |
|--|--|------------------------------------|------------|-------|
| 1. T | 2. F | 3. T | 4. T | 5. T |
| 6. F | 7. T | 8. T | 9. F | 10. T |
| 11. T | 12. T | 13. T | 14. F | 15. F |
| 16. 0.66 cm^{-1} | 17. O_2 | 18. increase | 19. higher | |
| 20. O_2 & H_2 | 21. Electrolyte concentration cell | | | |
| 22. $\text{Cr}_2\text{O}_7^{2-}(\text{aq.}), \text{Cr}^{3+}(\text{aq.}), \text{H}^+ \text{Pt}$ | | | | |
| 23. $\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$ | | | | |
| 24. $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{Hg}(\text{l}) + 2\text{Cl}^-(\text{aq.})$ | | | | |
| 25. $\Delta H = nF \left[T \left(\frac{dE}{dT} \right) - E \right]$ | 26. inert, i.e., should not interfere with net cell reaction | | | |
| 27. Salt bridge or porous partition | 28. zero | 29. E°_{red} cathode | | |
| 30. Amount, rate | 31. reduction process | 32. Oxygen | | |
| 33. $2.5 \times 96500 \text{ C}$ | | | | |

MIDDLE GAME

- | | | |
|--|--|---|
| Q.1 Eq. wt. = 107.3 | Q.2 $[\text{Cu}^{2+}] = 10^{-4} \text{ M}$ | Q.3 643.33amp, 190.5g |
| Q.4 43.456g | Q.5 265 Amp. hr. | Q.6 $E = 1.1 \text{ V}$ |
| Q.7 $E^\circ = -1.59 \text{ V}$, non-spontaneous | | Q.8 $K_{\text{sp}} = 1.1 \times 10^{-16}$ |
| Q.9 $\text{pH} = 6.61$ | Q.10 $E^0 = 0.71 \text{ V}$ | Q.11 $[\text{Br}^-] : [\text{Cl}^-] = 1 : 200$ |
| Q.12 $E^0 = -0.1511 \text{ V}$ | Q.13 $K_a = 6.74 \times 10^{-4}$ | Q.14 $[\text{Zn}^{2+}]/[\text{Cu}^{2+}] = 1.941 \times 10^{37}$ |
| Q.15 1.39V | Q.16 0.373V | Q.17 $K_f = 8.227 \times 10^{63}$ |
| Q.18 -0.46 V | Q.19 42.2 % | Q.20 (ii). 1.2V, (iii) 245.1 kJ |
| Q.21 -0.037 V | Q.22 A48.71 hour, $[\text{OH}^-] = 1.41 \text{ M}$ | |
| Q.23 $\text{V}(\text{O}_2) = 99.68 \text{ mL}$, $\text{V}(\text{H}_2) = 58.46 \text{ mL}$, Total vol. = 158.1 mL | | |
| Q.24 57.5894 gm | Q.25 315.36 A | Q.26 1.9 million year |
| Q.27 0.179 V | | |
| Q.28 0.372 V, -0.307 V | Q.29 $h = 2.12 \times 10^{-2}$, $K_h = 1.43 \times 10^{-5} \text{ M}$ | |
| Q.30 0.95 V | Q.31 $1.536 \times 10^{-5} \text{ M}^3$ | Q.32 0.1456 ampere |
| Q.33 3.29 cm | Q.34 $4.25 \times 10^{-2} \text{ metre}$ | Q.35 0.1934 gm/litre |

ZENITH

- | | | |
|--|---|--|
| Q.1 $1.21 \times 10^5 \text{ coulomb}$ | Q.2 $\text{Cu} = 98.88\%$, $\text{Fe} = 0.85\%$ | Q.3 1250 s, 0.064 M |
| Q.4 $K = 10^{268}$ | Q.5 $\text{Ti}^+ = 10^{-8}$; $\text{Co}^{3+} = 2 \times 10^{-8}$ | Q.6 1.66V |
| Q.7 -1.188 V | Q.8 10^{-2} | Q.9 5.24×10^{16} |
| Q.10 1.143V | Q.11 (a) -0.124 V , (b) 7.1, (c) calomel electrode | |
| Q.12 0.4414 V | Q.13 -0.167 V | Q.14 $K_{\text{SP}} = 7.682 \times 10^{-17}$ |
| Q.15 $2 \times 10^5 \text{ dm}^3$ | | |

SUHANA SAFAR

OBJECTIVE

Q.1	A	Q.2	C	Q.3	B	Q.4	A	Q.5	A
Q.6	B	Q.7	C	Q.8	B	Q.9	C	Q.10	A
Q.11	C	Q.12	B	Q.13	B				

SUBJECTIVE

Q.14 $E^0 = -0.22\text{N}$

Q.15 $\eta = 94.8\%$; Cathode : $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$, Anode : $\text{Mn}^{2+} \rightarrow \text{Mn}^{4+} + 2\text{e}^-$

Q.16 $W_{\text{Ag}} = 272.2\text{g}$, area = $1.02 \times 10^4 \text{ cm}^2$ Q.17 $K_c = 7.6 \times 10^{12}$ Q.18 $K_c = 6.26 \times 10^7$

Q.19 $K_{\text{sp}} = 2.287 \times 10^{-12} \text{ M}^{-3}$ Q.20 $7.95 \times 10^{-5} \text{ M}$

Q.21 decrease with time

Q.22 $\Delta H^0 = -49987 \text{ J mol}^{-1}$, $\Delta S^0 = -96.5 \text{ J mol}^{-1} \text{ K}^{-1}$, $s = 1.47 \times 10^{-5} \text{ M}$

Q.23 0.05 M Q.24 $K_c = 10^{10}$

Q.25 (a) $E^0 = 0.59 \text{ V}$, $\log_{10} K_{\text{sp}} = -10$
(b) $52.8, 10^{-6} \text{ moles}$