

SUPPORT STUDY MATERIAL

XI Chemistry

Study Material,
Support Material,
Study Notes and VBQ

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UNIT 1

SOME BASIC CONCEPTS OF CHEMISTRY

Chemistry: Chemistry is the branch of science that deals with the composition, structure and properties of matter. Chemistry is called the science of atoms and molecule

Branches of Chemistry

- Organic Chemistry -This branch deals with study of carbon compounds especially hydrocarbons and their derivatives.
- Inorganic Chemistry-This branch deals with the study of compounds of all other elements except carbon. It largely concerns itself with the study of minerals found in the Earth's crust.
- Physical Chemistry-The explanation of fundamental principles governing various chemical phenomena is the main concern of this branch. It is basically concerned with laws and theories of the different branches of chemistry.
- Industrial Chemistry-The chemistry involved in industrial processes is studied under this branch.
- Analytical Chemistry-This branch deals with the qualitative and quantitative analysis of various substances.
- Biochemistry-This branch deals with the chemical changes going on in the bodies of living organisms; plants and animals.
- Nuclear Chemistry-Nuclear reactions, such as nuclear fission, nuclear fusion, transmutation processes etc. are studied under this branch.

PROPERTIES OF MATTER AND THEIR MEASUREMENT--Every substance has unique or characteristic properties. These properties can be classified into two categories – **physical properties** and **chemical properties**.

Physical properties are those properties which can be measured or observed without changing the identity or the composition of the substance. E.g. colour, odour, melting point, boiling point, density etc.

The measurement or observation of **chemical properties** requires a chemical change to occur. e.g. Burning of Mg-ribbon in air

Chemical properties are characteristic reactions of different substances; these include acidity or basicity, combustibility etc. Many properties of matter such as length, area, volume, etc., are quantitative in nature.

Metric System was based on the decimal system.

The International System of Units (SI)

The International System of Units (in French Le Systeme International d'Unites—abbreviated as SI) was established by the 11th General Conference on Weights and Measures (CGPM from *Conference Generale des Poids et Mesures*). The SI system has seven *base units*

| Quantity | Unit | Symbol |
|---------------------|----------|--------|
| Length | metre | m |
| Mass | kilogram | kg |
| Time | second | s |
| Temperature | kelvin | K |
| Amount of substance | mole | mol |
| Electric current | ampere | A |
| Luminous intensity | candela | Cd |

Prefixes in SI system

| Multiple | Prefix | Symbol |
|------------|--------|--------|
| 10^{-12} | pico | p |
| 10^{-9} | nano | n |
| 10^{-6} | micro | μ |
| 10^{-3} | milli | m |
| 10^{-2} | centi | c |
| 10^{-1} | deci | d |
| 10 | deca | da |
| 10^2 | hecto | h |
| 10^3 | kilo | k |
| 10^6 | mega | M |
| 10^9 | giga | G |
| 10^{12} | tera | T |

Mass and Weight-- Mass of a substance is the amount of matter present in it while weight is the force exerted by gravity on an object. The mass of a substance is constant whereas its weight may vary from one place to another due to change in gravity. The mass of a substance can be determined very accurately by using an analytical balance

Volume-- Volume has the units of (length)³. So volume has units of m³ or cm³ or dm³. A common unit, litre (L) is not an SI unit, is used for measurement of volume of liquids. 1 L = 1000 mL, 1000 cm³ = 1 dm³

Density: Density of a substance is its amount of mass per unit volume. SI unit of density = SI unit of mass/SI unit of volume = kg/m³ or kg m⁻³. This unit is quite large and a chemist often expresses density in g cm⁻³.

Temperature-- There are three common scales to measure temperature — °C (degree celsius), °F (degree Fahrenheit) and K (kelvin). Here, K is the SI unit.

$${}^{\circ}\text{F} = \frac{9}{5}({}^{\circ}\text{C}) + 32$$

$$\text{K} = {}^{\circ}\text{C} + 273.15$$

Note—Temperature below 0 °C (i.e. negative values) are possible in Celsius scale but in Kelvin scale, negative temperature is not possible.

Scientific Notation

In which any number can be represented in the form $N \times 10^n$ (Where n is an exponent having positive or negative values and N can vary between 1 to 10).

e.g. We can write 232.508 as 2.32508×10^2 in scientific notation. Similarly, 0.00016 can be written as 1.6×10^{-4} .

Precision refers to the closeness of various measurements for the same quantity.

Accuracy is the agreement of a particular value to the true value of the result

Significant Figures

The reliability of a measurement is indicated by the number of digits used to represent it. To express it more accurately we express it with digits that are known with certainty. These are called as Significant figures. They contain all the certain digits plus one doubtful digit in a number.

Rules for Determining the Number of Significant Figures

- All non-zero digits are significant. For example, 6.9 has two significant figures, while 2.16 has three significant figures. The decimal place does not determine the number of significant figures.
- A zero becomes significant in case it comes in between non zero numbers. For example, 2.003 has four significant figures, 4.02 has three significant figures.
- Zeros at the beginning of a number are not significant. For example, 0.002 has one significant figure while 0.0045 has two significant figures.
- All zeros placed to the right of a number are significant. For example, 16.0 has three significant figures, while 16.00 has four significant figures. Zeros at the end of a number without decimal point are ambiguous.
- In exponential notations, the numerical portion represents the number of significant figures. For example, 0.00045 is expressed as 4.5×10^{-4} in terms of scientific notations. The number of significant figures in this number is 2, while in Avogadro's number (6.023×10^{23}) it is four.
- The decimal point does not count towards the number of significant figures. For example, the number 345601 has six significant figures but can be written in different ways, as 345.601 or 0.345601 or 3.45601 all having same number of significant figures.

Retention of Significant Figures - Rounding off Figures

The rounding off procedure is applied to retain the required number of significant figures.

1. If the digit coming after the desired number of significant figures happens to be more than 5, the preceding significant figure is increased by one, 4.317 is rounded off to 4.32.
2. If the digit involved is less than 5, it is neglected and the preceding significant figure remains unchanged, 4.312 is rounded off to 4.31.
3. If the digit happens to be 5, the last mentioned or preceding significant figure is increased by one only in case it happens to be odd. In case of even figure, the

preceding digit remains unchanged. 8.375 is rounded off to 8.38 while 8.365 is rounded off to 8.36.

Dimensional Analysis During calculations generally there is a need to convert units from one system to other. This is called **factor label method** or **unit factor method** or **dimensional analysis**.

For example- 5 feet and 2 inches (height of an Indian female) is to be converted in SI unit

$$1 \text{ inch} = 2.54 \times 10^{-2} \text{ m}$$

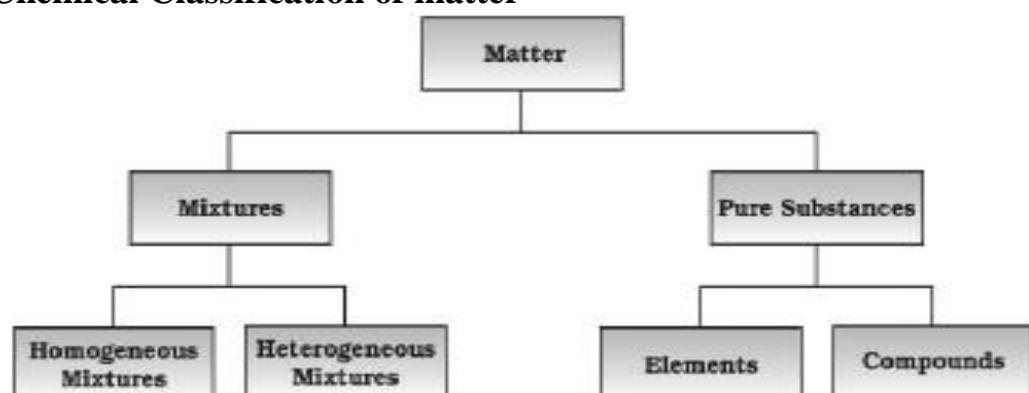
$$1 = \frac{2.54 \times 10^{-2} \text{ m}}{1 \text{ inch}} \text{ then, } 5 \text{ feet and } 2 \text{ inch} = 62 \text{ inch}$$

$$= 62 \text{ inch} \times \frac{2.54 \times 10^{-2} \text{ m}}{1 \text{ inch}} = 1.58 \text{ m}$$

Physical Classification of Matter

| Properties | Solid | Liquid | Gas |
|--|--|--|--|
| 1. volume | Definite | Definite | Indefinite |
| 2. Shape | Definite | Indefinite | Indefinite |
| 3. Inter molecular force of attraction | Very high | Moderate | Negligible / Very low |
| 4. arrangement of molecules | Orderly arranged | Free to move within the volume | Free to move everywhere |
| 5. Inter molecular space | Very small | Slightly greater | Very great |
| 7. Compressibility | Not compressible | Not compressible | Highly compressible |
| 8. Expansion on heating | Very little | Very little | Highly expand |
| 9. Rigidity | Very rigid | Not rigid known as fluid | Not rigid and known as fluid |
| 9. Fluidity | Can't flow | Can flow | Can flow |
| 10. Diffusion | They can diffuse due to kinetic energy of liquid/gases | Can diffuse And rate of diffusion is very fast | Can diffuse And rate of diffusion is very fast |

Chemical Classification of matter---



Elements

An element is the simplest form of matter that cannot be split into simpler substances or built from simpler substances by any ordinary chemical or physical method. There are 114 elements known to us, out of which 92 are naturally occurring while the rest have been prepared artificially.

Elements are further classified into metals, non-metals and metalloids.

Compounds

A compound is a pure substance made up of two or more elements combined in a definite proportion by mass, which could be split by suitable chemical methods.

Characteristics of compound

- Compounds always contain a definite proportion of the same elements by mass.
- The properties of compounds are totally different from the elements from which they are formed.
- Compounds are homogeneous.
- Compounds are broadly classified into inorganic and organic compounds. Inorganic compounds are those, which are obtained from non-living sources such as minerals. For example, common salt, marble and limestone. Organic compounds are those, which occur in living sources such as plants and animals. They all contain carbon. Common organic compounds are oils, wax, fats etc.

Mixtures

A mixture is a combination of two or more elements or compounds in any proportion so that the components do not lose their identity. Air is an example of a mixture

Mixtures are of two types, homogeneous and heterogeneous.

Homogeneous mixtures have the same composition throughout the sample. The components of such mixtures cannot be seen under a powerful microscope. They are also called solutions. Examples of homogeneous mixtures are air, seawater, gasoline, brass etc.

Heterogeneous mixtures consist of two or more parts (phases), which have different compositions. These mixtures have visible boundaries of separation between the different constituents and can be seen with the naked eye e.g., sand and salt, chalk powder in water etc.

LAWS OF CHEMICAL COMBINATIONS

Law of Conservation of Mass (Given by Antoine Lavoisier in 1789).

It states that matter (mass) can neither be created nor destroyed.

Law of Definite Proportions or Law of Constant Composition:

This law was proposed by Louis Proust in 1799, which states that:

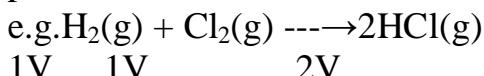
'A chemical compound always consists of the same elements combined together in the same ratio, irrespective of the method of preparation or the source from where it is taken'.

Law of Multiple Proportions Proposed by Dalton in 1803, this law states that:

'When two elements combine to form two or more compounds, then the different masses of one element, which combine with a fixed mass of the other, bear a simple ratio to one another'.

Gay Lussac's Law of Gaseous Volumes (Given by Gay Lussac in 1808.)

According to this law when gases combine or are produced in a chemical reaction they do so in a simple ratio by volume provided all gases are at same temperature and pressure.



All reactants and products have simple ratio 1:1:2.

Avogadro Law (In 1811, Given by Avogadro)

According to this law equal volumes of gases at the same temperature and pressure should contain equal number of molecules.

Dalton's Atomic Theory

- All substances are made up of tiny, indivisible particles called atoms.
- Atoms of the same element are identical in shape, size, mass and other properties.
- Atoms of different elements are different in all respects.
- Atom is the smallest unit that takes part in chemical combinations.
- Atoms combine with each other in simple whole number ratios to form compound atoms called molecules.
- Atoms cannot be created, divided or destroyed during any chemical or physical change.

Atoms and Molecules

The smallest particle of an element, which may or may not have independent existence is called an atom, while the smallest particle of a substance which is capable of independent existence is called a molecule.

Molecules are classified as homoatomic and heteroatomic. Homoatomic molecules are made up of the atoms of the same element and heteroatomic molecules are made up of the atoms of the different element have different atomicity (number of atoms in a molecule of an element) like monoatomic, diatomic, triatomic and polyatomic.

Atomic Mass Unit

One atomic mass unit is defined as a mass exactly equal to one twelfth the mass of one carbon -12 atom. And $1 \text{ amu} = 1.66056 \times 10^{-24} \text{ g}$.

Today, 'amu' has been replaced by 'u' which is known as unified mass.

Atomic Mass

Atomic mass of an element is defined as the average relative mass of an atom of an element as compared to the mass of an atom of carbon -12 taken as 12.

$$\text{Atomic mass} = \frac{\text{mass of an atom}}{1/12 \text{ mass of a carbon atom}({}^{12}\text{C})}$$

Gram Atomic Mass

The quantity of an element whose mass in grams is numerically equal to its atomic mass. In simple terms, atomic mass of an element expressed in grams is the gram atomic mass or gram atom.

For example, the atomic mass of oxygen = 16 amu

Therefore gram atomic mass of oxygen = 16 g

Molecular Mass

Molecular mass of a substance is defined as the average relative mass of its molecule as compared to the mass of an atom of C-12 taken as 12. It expresses as to how many times the molecule of a substance is heavier than 1/12th of the mass of an atom of carbon.

For example, a molecule of carbon dioxide is 44 times heavier than 1/12th of the mass of an atom of carbon. Therefore the molecular mass of CO₂ is 44 amu.

It is obtained by adding the atomic masses of all the atoms present in one molecule.

Gram Molecular Mass

A quantity of substance whose mass in grams is numerically equal to its molecular mass is called gram molecular mass. In simple terms, molecular mass of a substance expressed in grams is called gram molecular mass.

e.g., the molecular mass of oxygen = 32 amu

Therefore, gram molecular mass of oxygen = 32 g

Formula Mass-

Sum of atomic masses of the elements present in one formula unit of a compound. It is used for the ionic compounds.

Mole Concept.

Mole is defined as the amount of a substance, which contains the same number of chemical units (atoms, molecules, ions or electrons) as there are atoms in exactly 12 grams of pure carbon-12.

A mole represents a collection of 6.022×10^{23} (Avogadro's number) chemical units..

The mass of one mole of a substance in grams is called its molar mass.

Molar Volume

The volume occupied by one mole of any substance is called its molar volume. It is denoted by V_m. One mole of all gaseous substances at 273 K and 1 atm pressure occupies a volume equal to 22.4 litre or 22,400 mL. The unit of molar volume is litre per mol or millilitre per mol

PERCENTAGE COMPOSITION—

The mass percentage of each constituent element present in any compound is called its percentage composition

Mass % of the element = $\frac{\text{Mass of element in 1 molecule of the compound}}{\text{Molecular mass of the compound}} \times 100$

Empirical Formula and Molecular Formula—

An **empirical formula** represents the simplest whole number ratio of various atoms present in a compound. E.g. CH is the empirical formula of benzene.

The **molecular formula** shows the exact number of different types of atoms present in a molecule of a compound. E.g. C₆H₆ is the molecular formula of benzene.

Relationship between empirical and molecular formulae

The two formulas are related as Molecular formula = n × empirical formula

$$n = \frac{\text{Molecular mass}}{\text{empirical formula mass}}$$

Chemical Equation-

Shorthand representation of a chemical change in terms of symbols and formulae of the substances involved in the reaction is called chemical equation..

The substances that react among themselves to bring about the chemical changes are known as reactants, whereas the substances that are produced as a result of the chemical change, are known as products.

Limiting Reagent- The reactant which gets consumed first or limits the amount of product formed is known as **limiting reagent**

Reactions in Solutions-- The concentration of a solution can be expressed in any of the following ways.

1. **Mass Percent** is the mass of the solute in grams per 100 grams of the solution.

$$\text{Mass \% of the solute} = \frac{\text{Mass of the solute}}{\text{Mass of the solution}} \times 100$$

A 5 % solution of sodium chloride means that 5 g of NaCl is present in 100g of the solution.

2. **Volume percent** is the number of units of volume of the solute per 100 units of the volume of solution.

$$\text{Volume \% of the solute} = \frac{\text{Volume of the solute}}{\text{Volume of the solution}} \times 100$$

A 5 % (v/v) solution of ethyl alcohol contains 5 cm³ of alcohol in 100 cm³ of the solution

3. **Molarity** of the solution is defined as the number of moles of solute dissolved per litre (dm³) of the solution. It is denoted by the symbol M. Measurements in Molarity can change with the change in temperature because solutions expand or contract accordingly.

$$\text{Molarity of the solution} = \frac{\text{No. of moles of the solute}}{\text{Volume of the solution in litre}} = \frac{n}{V}$$

The Molarity of the solution can also be expressed in terms of mass and molar mass

$$\text{Molarity of the solution} = \frac{\text{Mass of the solute}}{\text{Molar mass of the solute} \times \text{volume of the solution in liter}}$$

In terms of weight, molarity of the substance can be expressed as:

$$\text{Molarity} = \frac{W_g}{M \text{ g mol}^{-1} \times V \text{ litre}} = \frac{W}{M \times V} \text{ mol/L}$$

Molarity equation

To calculate the volume of a definite solution required to prepare solution of other molarity, the following equation is used:

M₁V₁ = M₂V₂, where M₁= initial molarity, M₂= molarity of the new solution, V₁= initial volume and V₂= volume of the new solution.

4. **Molality**- Molality is defined as the number of moles of solute dissolved per 1000 g (1 kg) of solvent. Molality is expressed as 'm'.

$$\text{Molality} = \frac{\text{Moles of the solute}}{\text{Wt. of Solvent (in gm)}} \times 1000$$

5. Mole Fraction is the ratio of number of moles of one component to the total number of moles (solute and solvents) present in the solution. It is expressed as 'x'.

$$\text{Mole fraction of the solute} = \frac{\text{Moles of the solute}}{\text{Moles of solute} + \text{Moles of solvent}}$$

$$\text{Mole fraction of the solvent} = \frac{\text{Moles of the solvent}}{\text{Moles of solute} + \text{Moles of solvent}}$$

$$\text{Mole fraction of the solute} + \text{Mole fraction of solvent} = 1$$

One Mark questions with answers

1. What is the significant figures in 1.050×10^4 ?

Ans. Four

2. What is the S.I. unit of Density?

Ans. Kg m^{-3}

3. What do mean by Mole fraction?

Ans. Mole Fraction is the ratio of number of moles of one component to the total number of moles (solute and solvents) present in the solution. It is expressed as 'x'.

4. Round off up to 3 significant figure (a) 1.235 (b) 1.225

Ans. (a) 1.24 (b) 1.22

5. What is AZT?

Ans. Azidothymidine.

6. What is limiting reagent?

Ans. The reactant which gets consumed first or limits the amount of product formed is known as **limiting reagent**

7. What is the relation between temperature in degree Celsius and degree fahrenheit?

Ans.

$${}^{\circ}\text{F} = \frac{9}{5}({}^{\circ}\text{C}) + 32$$

8. Define one mole?

Ans. One mole is the amount of a substance that contains as many particles as there are atoms in exactly 12 g of the carbon-12.

9. Calculate the formula mass calcium chloride.

Ans. Formula mass of $\text{CaCl}_2 = 40+2 \times 35.5 = 40+71 = 111 \text{ u}$

10. What is the law called which deals with the ratios of the volumes of the gaseous reactants and products?

Ans. Gay Lussac's law of gaseous volumes.

Two Marks questions with answers

1. Give the two points of differences between homogeneous and heterogeneous mixtures.

Ans.

| Homogeneous mixture | Heterogeneous mixture |
|--|--|
| <ol style="list-style-type: none"> Homogeneous mixtures have the same composition throughout the sample. The components of such mixtures cannot be seen under a powerful microscope. | <ol style="list-style-type: none"> Heterogeneous mixtures consist of two or more parts (phases), which have different compositions. These mixtures have visible boundaries of separation between the different constituents and can be seen with the naked eye |

2. Copper oxide obtained by heating copper carbonate or copper nitrate contains copper and oxygen in the same ration by mass. Which law is illustrated by this observation? State the law.

Ans. **Law of Definite Proportions** This law states that: A chemical compound always consists of the same elements combined together in the same ratio, irrespective of the method of preparation or the source from where it is taken.

3. Write the empirical formula of the following:

(a) N_2O_4 (b) $\text{C}_6\text{H}_{12}\text{O}_6$ (c) H_2O (d) H_2O_2

Ans. (a) NO_2 (b) CH_2O (c) H_2O (d) HO

4. Briefly explain the difference between precision and accuracy.

Ans. Precision refers to the closeness of various measurements for the same quantity. However, accuracy is the agreement of a particular value to the true value of the result.

5. Define the law of multiple proportions. Explain it with one example.

Ans. When two elements combine to form two or more compounds, then the different masses of one element, which combine with a fixed mass of the other, bear a simple ratio to one another. For example- carbon combines with oxygen to form two compounds CO and CO_2 .

| Compound | CO | CO_2 |
|-----------|----|---------------|
| Mass of C | 12 | 12 |
| Mass of O | 16 | 32 |

Masses of oxygen which combine with a fixed mass of carbon (12g) bear a simple ratio of 16:32 or 1:2.

6. Chlorine has two isotopes of atomic mass units 34.97 and 36.97. The relative abundance of the isotopes is 0.755 and 0.245 respectively. Find the average atomic mass of chlorine.

Ans. Average atomic mass = $34.97 \times 0.755 + 36.97 \times 0.245 = 35.46 \text{ u}$

7. Calculate the percentage composition of water.

Ans. Mass % of an element = $\frac{\text{mass of that element in the compound}}{\text{molar mass of the compound}} \times 100$

Molar mass of water = 18.02 g

Mass % of hydrogen = $\frac{2 \times 1.008 \times 100}{18.02}$

$$= 11.18$$

Mass % of oxygen = $\frac{16.00 \times 100}{18.02} = 88.79$

8. State the number of significant figures in each of the following:

- (i) 208.91 (ii) 0.00456 (iii) 453 (iv) 0.346

Ans.

- (i) 208.91 has five significant figures.
(ii) 0.00456 has three significant figures.
(iii) 453 has three significant figures.
(iv) 0.346 has three significant figures.

8. Express the results of the following calculations to the appropriate number of significant figures.

$$(i) \frac{3.24 \times 0.08666}{5.006} \quad (ii) \frac{(1.36 \times 10^{-4})(0.5)}{2.6}$$

Ans.

$$\begin{aligned}(i) \frac{3.24 \times 0.08666}{5.006} &= 0.05608 = 0.0561 \\(ii) \frac{(1.36 \times 10^{-4})(0.5)}{2.6} &= 0.2615 \times 10^{-4} = 0.3 \times 10^{-4}\end{aligned}$$

9. How are 0.50 mol Na₂CO₃ and 0.50 M Na₂CO₃ different?

Ans. Molar mass of Na₂CO₃ = 2 x 23 + 12 + 3 x 16 = 106 g / mol

0.50 mol Na₂CO₃ means 0.50 x 106 = 53 g

0.50 M Na₂CO₃ means 0.50 mol i.e. 53 g of Na₂CO₃ are present in 1 L of the solution.

Three Marks questions with answers-

1. What is unit factor method? Express the following in SI units - 93 million miles (distance between earth and sun)

Ans. Method to convert units from one system to other is called unit factor method.

93 million miles = 93 x 10⁶ miles

1 mile = 1.60934 km = 1.60934 x 10³ m

$$1 = \frac{1.60934 \times 10^3 \text{ m}}{1 \text{ mile}}$$

$$\begin{aligned}93 \text{ million mile} &= 93 \times 10^6 \text{ mile} \times \frac{1.60934 \times 10^3 \text{ m}}{1 \text{ mile}} \\&= 1.5 \times 10^{11} \text{ m}\end{aligned}$$

2. Write the three points of difference between compound and mixture.

Ans.

| Compound | Mixture |
|--|--|
| Constituents are always present in a fixed ratio by mass | Constituents may be present in any ratio |
| May or may not be homogeneous in nature | Always homogeneous in nature |
| Constituents can be easily separated | Constituents cannot be easily |

| | |
|--|---|
| by simple mechanical means | separated by simple mechanical means |
| Properties are midway between those of its constituents. | Properties are entirely different from those of its constituents. |

3. What do mean by gram atomic mass. One million silver atoms weigh 1.79×10^{16} g. Calculate the gram atomic mass of silver.

Ans. atomic mass of an element expressed in grams is the gram atomic mass

$$\text{Number of silver atoms} = 1 \text{ million} = 1 \times 10^6$$

$$\text{Mass of one million Ag atoms} = 1.79 \times 10^{16} \text{ g}$$

$$\begin{aligned}\text{Mass of } 6.023 \times 10^{23} \text{ atoms of silver} &= \frac{1.79 \times 10^{16} \text{ g}}{1 \times 10^6} \times 6.023 \times 10^{23} \\ &= 107.8 \text{ g}\end{aligned}$$

4. What is the percentage of carbon, hydrogen and oxygen in ethanol?

Ans. Molecular formula of ethanol is : $\text{C}_2\text{H}_5\text{OH}$

Molar mass of ethanol is : $(212.01 + 61.008 + 16.00) \text{ g} = 46.068 \text{ g}$

$$\text{Mass per cent of carbon} = (24.02 \text{ g} / 46.068 \text{ g}) \times 100 = 52.14\%$$

$$\begin{aligned}\text{Mass per cent of hydrogen} &= (6.048 \text{ g} / 46.068 \text{ g}) \times 100 = 13.13\% \\ \text{Mass per cent of oxygen} &= (16.00 \text{ g} / 46.068 \text{ g}) \times 100 = 34.73\%\end{aligned}$$

5. What do mean by molarity .Calculate the molarity of NaOH in the solution prepared by dissolving its 4 g in enough water to form 250 mL of the solution.

Ans. The number of moles of solute dissolved per litre (dm^3) of the solution is called molarity

Since molarity (M) = No. of moles of solute / Volume of solution in litres

$$= (\text{Mass of NaOH} / \text{Molar mass of NaOH}) / 0.250 \text{ L}$$

$$= (4 \text{ g} / 40 \text{ g} / 0.1 \text{ mol}) / 0.250 \text{ L} = 0.1 \text{ mol} / 0.250 \text{ L}$$

$$= 0.4 \text{ mol L}^{-1}$$

$$= 0.4 \text{ M}$$

6. Classify the following as pure substances or mixture-

- (a) ethyl alcohol (b) oxygen (c) blood (d) carbon (e) steel (f)
distilled water

Ans. Pure substance- ethyl alcohol ,oxygen , carbon, distilled water

Mixture- blood, steel

7. What are the rules for rounding off?

Ans.1. If the digit coming after the desired number of significant figures happens to be more than 5, the preceding significant figure is increased by one,

2. If the digit involved is less than 5, it is neglected and the preceding significant figure remains unchanged,

3. If the digit happens to be 5, the last mentioned or preceding significant figure is increased by one only in case it happens to be odd. In case of even figure, the preceding digit remains unchanged.
8. Define –(a) Average atomic mass (b) Molecular mass (c) Formula mass
- Ans. (a) Average atomic mass- Atomic mass of an element is defined as the average relative mass of an atom of an element as compared to the mass of an atom of carbon -12 taken as 12.
- (b) Molecular mass- it is sum of atomic masses of the elements present in a molecule.
- (c) Formula mass- it is sum of atomic masses of the elements present in a formula unit of a compound.

9. Express the following in the scientific notation with 2 significant figures-

(a) 0.0048 (b) 234,000 (c) 200.0

Ans. (a) 4.8×10^{-3} (b) 2.3×10^5 (c) 2.0×10^2

10. Calculate the number of atoms in each of the following (i) 52 moles of Ar

(ii) 52 u of He (iii) 52 g of He

Ans. (i) 1 mole of Ar = 6.022×10^{23} atoms of Ar

$$\therefore 52 \text{ mol of Ar} = 52 \times 6.022 \times 10^{23} \text{ atoms of Ar}$$

$$= 3.131 \times 10^{25} \text{ atoms of Ar}$$

(ii) 1 atom of He = 4 u of He

Or,

4 u of He = 1 atom of He

$$1 \text{ u of He} = 1/4 \text{ atom of He}$$

$$52 \text{ u of He} = 52/4 \text{ atom of He}$$

$$= 13 \text{ atoms of He}$$

(iii) Molar mass of He = 4 g/mol

$$4 \text{ g of He contains} = 6.022 \times 10^{23} \text{ atoms of He}$$

$$52 \text{ g of He contains} = \frac{6.022 \times 10^{23} \times 52}{4} = 78.286 \times 10^{23} \text{ atoms of He}$$

Five Marks questions with answers-

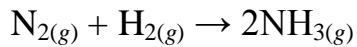
1. What is the difference between empirical and molecular formula? A compound contains 4.07 % hydrogen, 24.27 % carbon and 71.65 % chlorine. Its molar mass is 98.96 g. What are its empirical and molecular formulas?

Ans. An empirical formula represents the simplest whole number ration of various atoms present in a compound whereas the molecular formula shows the exact number of different types of atoms present in a molecule of a compound.

| Name of element | Percentage of elements | Step-1 Conversion of mass per cent to grams. | Step 2. number moles of each element | Step 3. Divide the mole value by the smallest number |
|-----------------|------------------------|--|--------------------------------------|--|
| C | 24.27% | 24.27g | 24.27/12 = 2.0225 | 2.0225/2.018 = 1 |
| H | 4.07% | 4.07g | 4.07/1 = 4.07 | 4.07/2.018 = 2 |
| Cl | 71.65% | 71.65g | 71.65/35.5 = 2.018 | 2.018/2.018 = 1 |

The empirical formula of the above compound is CH₂Cl.
 empirical formula mass is $12 + (1 \times 2) + 35.5 = 49.5$
 $n = \text{molecular mass} / \text{empirical formula mass} = 98.96 / 49.5 = 2$
 Hence molecular formula is C₂H₄Cl₂

2. Dinitrogen and dihydrogen react with each other to produce ammonia according to the following chemical equation:



- (i) Calculate the mass of ammonia produced if 2.00×10^3 g dinitrogen reacts with 1.00×10^3 g of dihydrogen.
- (ii) Will any of the two reactants remain unreacted?
- (iii) If yes, which one and what would be its mass?

Ans. (i) Balancing the given chemical equation, $\text{N}_{2(g)} + 3\text{H}_{2(g)} \longrightarrow 2\text{NH}_{3(g)}$

From the equation, 1 mole (28 g) of dinitrogen reacts with 3 mole (6 g) of dihydrogen to give 2 mole (34 g) of ammonia.

$\Rightarrow 2.00 \times 10^3$ g of dinitrogen will react with $\frac{6 \text{ g}}{28 \text{ g}} \times 2.00 \times 10^3$ g dihydrogen i.e.,

2.00×10^3 g of dinitrogen will react with 428.6 g of dihydrogen.

Given,

$$\text{Amount of dihydrogen} = 1.00 \times 10^3 \text{ g}$$

Hence, N₂ is the limiting reagent.

$\therefore 28 \text{ g of N}_2 \text{ produces } 34 \text{ g of NH}_3$.

Hence, mass of ammonia produced by 2000 g of N₂ $= \frac{34 \text{ g}}{28 \text{ g}} \times 2000 \text{ g}$

$$= 2428.57 \text{ g}$$

(ii) N₂ is the limiting reagent and H₂ is the excess reagent. Hence, H₂ will remain unreacted.

$$\begin{aligned}\text{(iii) Mass of dihydrogen left unreacted} &= 1.00 \times 10^3 \text{ g} - 428.6 \text{ g} \\ &= 571.4 \text{ g}\end{aligned}$$

3. A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide, 0.690 g of water and no other products. A volume of 10.0 L (measured at STP) of this welding gas is found to weigh 11.6 g. Calculate (i) empirical formula, (ii) molar mass of the gas, and (iii) molecular formula.

Ans. (i) 1 mole (44 g) of CO₂ contains 12 g of carbon.

$$\begin{aligned}3.38 \text{ g of CO}_2 \text{ will contain carbon} &= \frac{12 \text{ g}}{44 \text{ g}} \times 3.38 \text{ g} \\ &= 0.9217 \text{ g}\end{aligned}$$

18 g of water contains 2 g of hydrogen.

$$\begin{aligned}0.690 \text{ g of water will contain hydrogen} &= \frac{2 \text{ g}}{18 \text{ g}} \times 0.690 \\ &= 0.0767 \text{ g}\end{aligned}$$

Since carbon and hydrogen are the only constituents of the compound, the total mass of the compound is: = 0.9217 g + 0.0767 g = 0.9984 g

$$\begin{aligned}\text{Percent of C in the compound} &= \frac{0.9217 \text{ g}}{0.9984 \text{ g}} \times 100 \\ &= 92.32\%\end{aligned}$$

$$\begin{aligned}\text{Percent of H in the compound} &= \frac{0.0767 \text{ g}}{0.9984 \text{ g}} \times 100 \\ &= 7.68\%\end{aligned}$$

$$\begin{aligned}\text{Moles of carbon in the compound} &= \frac{92.32}{12.00} \\ &= 7.69\end{aligned}$$

$$\begin{aligned}\text{Moles of hydrogen in the compound} &= \frac{7.68}{1} \\ &= 7.68\end{aligned}$$

Ratio of carbon to hydrogen in the compound = 7.69 : 7.68 = 1 : 1

Hence, the empirical formula of the gas is CH.

(ii) Given,

Weight of 10.0L of the gas (at S.T.P) = 11.6 g

$$\begin{aligned}\text{Weight of 22.4 L of gas at STP} &= \frac{11.6 \text{ g}}{10.0 \text{ L}} \times 22.4 \text{ L} \\ &= 25.984 \text{ g} \approx 26 \text{ g}\end{aligned}$$

Hence, the molar mass of the gas is 26 g.

(iii) Empirical formula mass of CH = $12 + 1 = 13$ g

$$n = \frac{\text{Molar mass of gas}}{\text{Empirical formula mass of gas}}$$

$$= \frac{26\text{g}}{13\text{g}}$$

$$n = 2$$

\therefore Molecular formula of gas = $(\text{CH})_n = \text{C}_2\text{H}_2$

HOTS (Higher Order Thinking Skills)

1. What is the difference between 160 cm and 160.0 cm

Ans. 160 has three significant figures while 160.0 has four significant figures. Hence, 160.0 represents greater accuracy.

2. In the combustion of methane, what is the limiting reactant and why?

Ans. Methane is the limiting reactant because the other reactant is oxygen of the air which is always present in excess. Thus, the amounts of CO₂ and H₂O formed depend upon the amount of methane burnt.

3. A compound made up of two elements A and B has A = 70 %, B = 30 %. Their relative number of moles in the compound are 1.25 and 1.88. calculate

a. Atomic masses of the elements A and B

b. Molecular formula of the compound , if its molecular mass is found to be 160

Ans. Relative no. of moles of an element = % of the element

Atomic mass

Or atomic mass = % of the element = 70 = 56

Relative no. of moles 1.25

Atomic mass of B = $30/1.88 = 16$

Calculation of Empirical formula

| Element | Relative no. of moles | Simplest molar ratio | Simplest whole no. molar ratio |
|---------|-----------------------|----------------------|--------------------------------|
| A | 1.25 | $1.25/1.25 = 1$ | 2 |
| B | 1.88 | $1.88/1.25 = 1.5$ | 3 |

Empirical formula = A₂B₃

Calculation of molecular formula-

Empirical formula mass = $2 \times 56 + 3 \times 16 = 160$

$n = \text{molecular mass} / \text{Empirical formula mass} = 160/160 = 1$

Molecular formula = A₂B₃

CHAPTER 2

STRUCTURE OF ATOM

- Atom is the smallest indivisible particle of the matter. Atom is made of electron, proton and neutrons.

| PARTICLE | ELECTRON | PROTON | NEUTRON |
|-------------------------|-------------------------------|-------------------------------|------------------------------|
| Discovery | Sir. J. J. Thomson (1869) | Goldstein (1886) | Chadwick (1932) |
| Nature of charge | Negative | Positive | Neutral |
| Amount of charge | 1.6×10^{-19} Coloumb | 1.6×10^{-19} Coloumb | 0 |
| Mass | 9.11×10^{-31} kg | 1.672614×10^{-27} kg | 1.67492×10^{-27} kg |

- Electrons were discovered using cathode ray discharge tube experiment.
- Nucleus was discovered by Rutherford in 1911.
- Cathode ray discharge tube experiment: A cathode ray discharge tube made of glass is taken with two electrodes. At very low pressure and high voltage, current starts flowing through a stream of particles moving in the tube from cathode to anode. These rays were called cathode rays. When a perforated anode was taken, the cathode rays struck the other end of the glass tube at the fluorescent coating and a bright spot on the coating was developed.

Results:

- Cathode rays consist of negatively charged electrons.
 - Cathode rays themselves are not visible but their behavior can be observed with help of fluorescent or phosphorescent materials.
 - In absence of electrical or magnetic field cathode rays travel in straight lines
 - In presence of electrical or magnetic field, behaviour of cathode rays is similar to that shown by electrons
 - The characteristics of the cathode rays do not depend upon the material of the electrodes and the nature of the gas present in the cathode ray tube.
- Charge to mass ratio of an electron was determined by Thomson. The charge to mass ratio of an electron as $1.758820 \times 10^{11} \text{ C kg}^{-1}$
 - Charge on an electron was determined by R A Millikan by using an oil drop experiment. The value of the charge on an electron is $-1.6 \times 10^{-19} \text{ C}$.
 - The mass on an electron was determined by combining the results of Thomson's experiment and Millikan's oil drop experiment. The mass of an electron was determined to be $9.1094 \times 10^{-31} \text{ kg}$.
 - Discovery of protons and canal rays:** Modified cathode ray tube experiment was carried out which led to the discovery of protons.
 - Characteristics of positively charged particles:
 - Charge to mass ratio of particles depends on gas from which these originate

- b. The positively charged particles depend upon the nature of gas present in the cathode ray discharge tube
- c. Some of the positively charged particles carry a multiple of fundamental of electrical charge.
- d. Behaviour of positively charged particles in electrical or magnetic field is opposite to that observed for cathode rays

- **Neutrons** were discovered by James Chadwick by bombarding a thin sheet of beryllium by α - particles. They are electrically neutral particles having a mass slightly greater than that of the protons.
- Atomic number (Z) : the number of protons present in the nucleus (Moseley 1913).
- **Mass Number (A)** : Sum of the number of protons and neutrons present in the nucleus.
- **Thomson model of an atom:** This model proposed that atom is considered as a uniform positively charged sphere and electrons are embedded in it. An important feature of Thomson model of an atom was that mass of atom is considered to be evenly spread over the atom. Thomson model of atom is also called as Plum pudding, raisin pudding or watermelon model. Thomson model of atom was discarded because it could not explain certain experimental results like the scattering of α - particles by thin metal foils.
- **Observations from α - particles scattering experiment by Rutherford:**
 - a. Most of the α - particles passed through gold foil un deflected
 - b. A small fraction of α - particles got deflected through small angles
 - c. Very few α - particles did not pass through foil but suffered large deflection nearly 180°
- **Conclusions Rutherford drew from α - particles scattering experiment:**
 - a. Since most of the α - particles passed through foil undeflected, it means most of the space in atom is empty
 - b. Since some of the α - particles are deflected to certain angles, it means that there is positively mass present in atom
 - c. Since only some of the α - particles suffered large deflections, the positively charged mass must be occupying very small space
 - d. Strong deflections or even bouncing back of α - particles from metal foil were due to direct collision with positively charged mass in atom
- **Rutherford's model of atom:** This model explained that atom consists of nucleus which is concentrated in a very small volume. The nucleus comprises of protons and neutrons. The electrons revolve around the nucleus in fixed orbits. Electrons and nucleus are held together by electrostatic forces of attraction.
- **Drawbacks of Rutherford's model of atom:**
 - a. According to Rutherford's model of atom, electrons which are negatively charged particles revolve around the nucleus in fixed orbits. Thus,

- b. the electrons undergo acceleration. According to electromagnetic theory of Maxwell, a charged particle undergoing acceleration should emit electromagnetic radiation. Thus, an electron in an orbit should emit radiation. Thus, the orbit should shrink. But this does not happen.
- c. The model does not give any information about how electrons are redistributed around nucleus and what are energies of these electrons
- **Isotopes:** These are the atoms of the same element having the same atomic number but different mass number. e.g. ${}_1^1\text{H}$, ${}_1^2\text{H}$, ${}_1^3\text{H}$
- **Isobars:** Isobars are the atoms of different elements having the same mass number but different atomic numbers. e.g. ${}_{18}^{40}\text{Ar}$, ${}_{20}^{40}\text{Ca}$
- **Isoelectronic species:** These are those species which have the same number of electrons.
- **Electromagnetic radiations:** The radiations which are associated with electrical and magnetic fields are called electromagnetic radiations. When an electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the form of waves. These waves are called electromagnetic waves or electromagnetic radiations.
- **Properties of electromagnetic radiations:**
 - a. Oscillating electric and magnetic field are produced by oscillating charged particles. These fields are perpendicular to each other and both are perpendicular to the direction of propagation of the wave.
 - b. They do not need a medium to travel. That means they can even travel in vacuum.
- **Characteristics of electromagnetic radiations:**
 - a. **Wavelength:** It may be defined as the distance between two neighbouring crests or troughs of wave as shown. It is denoted by λ .
 - b. **Frequency (v):** It may be defined as the number of waves which pass through a particular point in one second.
 - c. **Velocity (v):** It is defined as the distance travelled by a wave in one second. In vacuum all types of electromagnetic radiations travel with the same velocity. Its value is $3 \times 10^8 \text{ m sec}^{-1}$. It is denoted by v
 - d. **Wave number:** Wave number (\bar{v}) is defined as the number of wavelengths per unit length.
- Velocity = frequency \times wavelength $c = v\lambda$
- **Planck's Quantum Theory-**
 - The radiant energy is emitted or absorbed not continuously but discontinuously in the form of small discrete packets of energy called 'quantum'. In case of light, the quantum of energy is called a 'photon'
 - The energy of each quantum is directly proportional to the frequency of the radiation, i.e. $E \propto v$ or $E = hv$ where h = Planck's constant = $6.626 \times 10^{-34} \text{ Js}$
 - Energy is always emitted or absorbed as integral multiple of this quantum. $E = nhv$ Where $n=1,2,3,4,\dots$

- **Black body:** An ideal body, which emits and absorbs all frequencies, is called a black body. The radiation emitted by such a body is called black body radiation.
- **Photoelectric effect:** The phenomenon of ejection of electrons from the surface of metal when light of suitable frequency strikes it is called photoelectric effect. The ejected electrons are called photoelectrons.
- Experimental results observed for the experiment of Photoelectric effect-
 - When beam of light falls on a metal surface electrons are ejected immediately.
 - Number of electrons ejected is proportional to intensity or brightness of light
 - Threshold frequency (v_0): For each metal there is a characteristic minimum frequency below which photoelectric effect is not observed. This is called threshold frequency.
 - If frequency of light is less than the threshold frequency there is no ejection of electrons no matter how long it falls on surface or how high is its intensity.
- Photoelectric work function (W_0): The minimum energy required to eject electrons is called photoelectric work function. $W_0 = h\nu_0$
- Energy of the ejected electrons :

$$h(\nu - \nu_0) = \frac{1}{2}m_e v^2$$
- Dual behavior of electromagnetic radiation- The light possesses both particle and wave like properties, i.e., light has dual behavior. whenever radiation interacts with matter, it displays particle like properties.(Black body radiation and photoelectric effect) Wave like properties are exhibited when it propagates(interference and diffraction)
- When a white light is passed through a prism, it splits into a series of coloured bands known as spectrum.
- Spectrum is of two types: continuous and line spectrum
 - a. The spectrum which consists of all the wavelengths is called continuous spectrum.
 - b. A spectrum in which only specific wavelengths are present is known as a line spectrum. It has bright lines with dark spaces between them.
- Electromagnetic spectrum is a continuous spectrum. It consists of a range of electromagnetic radiations arranged in the order of increasing wavelengths or decreasing frequencies. It extends from radio waves to gamma rays.
- Spectrum is also classified as emission and line spectrum.
 - Emission spectrum: The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum.
 - Absorption spectrum is the spectrum obtained when radiation is passed through a sample of material. The sample absorbs radiation of

certain wavelengths. The wavelengths which are absorbed are missing and come as dark lines.

- The study of emission or absorption spectra is referred as spectroscopy.
- Spectral Lines for atomic hydrogen:

| Series | n₁ | n₂ | Spectral Region |
|---------------|----------------------|----------------------|------------------------|
| Lyman | 1 | 2, 3, 4, 5 ... | Ultraviolet |
| Balmer | 2 | 3, 4, 5 ... | Visible |
| Paschen | 3 | 4, 5 ... | Infrared |
| Brackett | 4 | 5, 6 ... | Infrared |
| Pfund | 5 | 6, 7... | Infrared |

- Rydberg equation

$$\bar{v} = 109,677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1}$$

$$R = \text{Rydberg's constant} = 109677 \text{ cm}^{-1}$$

- Bohr's model for hydrogen atom:**

- An electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called orbits or energy levels. These orbits are arranged concentrically around the nucleus.
- As long as an electron remains in a particular orbit, it does not lose or gain energy and its energy remains constant.
- When transition occurs between two stationary states that differ in energy, the frequency of the radiation absorbed or emitted can be calculated

$$v = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

- An electron can move only in those orbits for which its angular momentum is an integral multiple of $h/2\pi$

$$m_e v r = n \cdot \frac{h}{2\pi} \quad n = 1, 2, 3, \dots$$

- The radius of the n th orbit is given by $r_n = 52.9 \text{ pm} \times \frac{n^2}{Z}$
- energy of electron in n th orbit is :

$$E_n = -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2} \right) \text{ J}$$

- Limitations of Bohr's model of atom:**
 - Bohr's model failed to account for the finer details of the hydrogen spectrum.
 - Bohr's model was also unable to explain spectrum of atoms containing more than one electron.
- Dual behavior of matter:** de Broglie proposed that matter exhibits dual behavior i.e. matter shows both particle and wave nature. de Broglie's relation is

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

- **Heisenberg's uncertainty principle:** It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron. The product of their uncertainties is always equal to or greater than $h/4\pi$.

Mathematically $\Delta x \times \Delta p \geq \frac{h}{4\pi}$
 where Δx = uncertainty in position,
 Δp = uncertainty in momentum

- Heisenberg's uncertainty principle rules out the existence of definite paths or trajectories of electrons and other similar particles
- Failure of Bohr's model:
 - a. It ignores the dual behavior of matter.
 - b. It contradicts Heisenberg's uncertainty principle.
- Classical mechanics is based on Newton's laws of motion. It successfully describes the motion of macroscopic particles but fails in the case of microscopic particles.

Reason: Classical mechanics ignores the concept of dual behaviour of matter especially for sub-atomic particles and the Heisenberg's uncertainty principle.

- **Quantum mechanics** is a theoretical science that deals with the study of the motions of the microscopic objects that have both observable wave like and particle like properties.
- Quantum mechanics is based on a fundamental equation which is called Schrodinger equation.
- Schrodinger's equation: For a system (such as an atom or a molecule whose energy does not change with time) the Schrödinger equation is written as:

$$\hat{H}\Psi = E\Psi$$

\hat{H} is the Hamiltonian operator

E is the total energy of the system

Ψ represents the wave function which is the amplitude of the electron

Wave

- When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) of the electron associated with each energy level. Out of the possible values, only certain solutions are permitted. Each permitted solution is highly significant as it corresponds to a definite energy state. Thus, we can say that energy is quantized.
- Ψ gives us the amplitude of wave. The value of Ψ has no physical significance.
- Ψ^2 gives us the region in which the probability of finding an electron is maximum. It is called probability density.

- Orbital: The region of space around the nucleus where the probability of finding an electron is maximum is called an orbital.
- Quantum numbers: There are a set of four quantum numbers which specify the energy, size, shape and orientation of an orbital. To specify an orbital only three quantum numbers are required while to specify an electron all four quantum numbers are required.
- **Principal quantum number (n):** It identifies shell, determines sizes and

| N | 1 | 2 | 3 | 4 |
|---|---|---|----|----|
| Shell no.: | K | L | M | N |
| Total number of orbitals in a shell = n^2 | 1 | 4 | 9 | 16 |
| Maximum number of electrons = $2n^2$ | 2 | 8 | 18 | 32 |

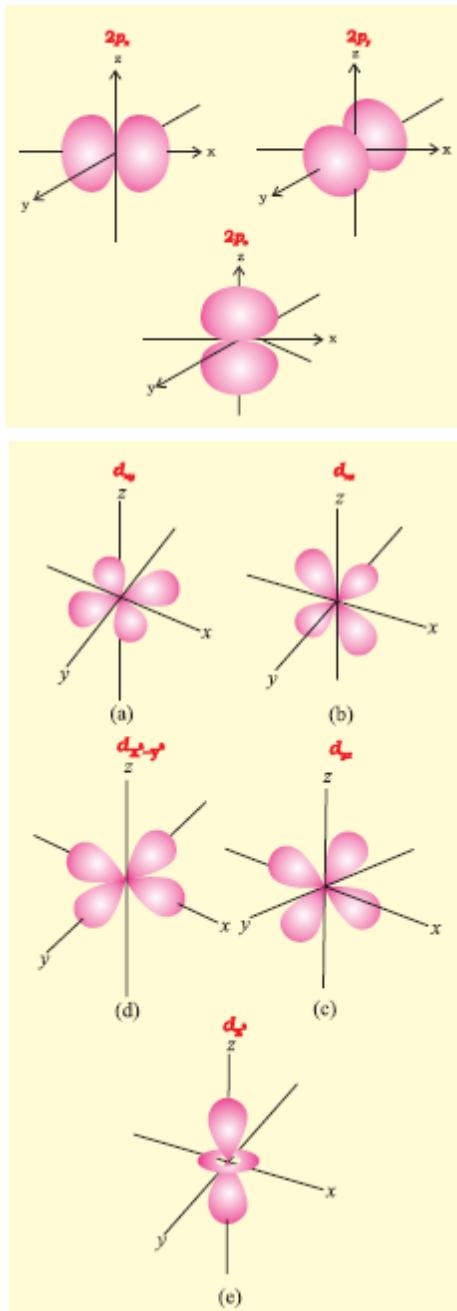
energy of orbitals

- **Azimuthal quantum number (l):** Azimuthal quantum number. 'l' is also known as orbital angular momentum or subsidiary quantum number. It identifies sub-shell, determines the shape of orbitals, energy of orbitals in multi-electron atoms along with principal quantum number and orbital angular momentum, i.e., $\sqrt{l(l+1)} \frac{h}{2\pi}$. The number of orbitals in a subshell = $2l + 1$. For a given value of n, it can have n values ranging from 0 to n-1. Total number of subshells in a particular shell is equal to the value of n.

| Subshell notation | s | p | d | f | g |
|--------------------|---|---|---|---|---|
| Value of 'l' | 0 | 1 | 2 | 3 | 4 |
| Number of orbitals | 1 | 3 | 5 | 7 | 9 |

- **Magnetic quantum number or Magnetic orbital quantum number (ml):** It gives information about the spatial orientation of the orbital with respect to standard set of co-ordinate axis. For any sub-shell (defined by 'l' value) $2l+1$ values of ml are possible. For each value of l, $m_l = -l, -(l-1), -(l-2) \dots 0, 1 \dots (l-2), (l-1), l$
- **Electron spin quantum number (ms):** It refers to orientation of the spin of the electron. It can have two values $+1/2$ and $-1/2$. $+1/2$ identifies the clockwise spin and $-1/2$ identifies the anti-clockwise spin.
- The region where this probability density function reduces to zero is called nodal surfaces or simply nodes.
- Radial nodes: Radial nodes occur when the probability density of wave function for the electron is zero on a spherical surface of a particular radius. Number of radial nodes = $n - 1 - 1$
- Angular nodes: Angular nodes occur when the probability density wavefunction for the electron is zero along the directions specified by a particular angle. Number of angular nodes = 1
- Total number of nodes = $n - 1$

- Degenerate orbitals: Orbitals having the same energy are called degenerate orbitals.
- Shape of p and d-orbitals



- **Shielding effect or screening effect:** Due to the presence of electrons in the inner shells, the electron in the outer shell will not experience the full positive charge on the nucleus.
So, due to the screening effect, the net positive charge experienced by the electron from the nucleus is lowered and is known as effective nuclear charge. Effective nuclear charge experienced by the orbital decreases with increase of azimuthal quantum number (l).
- **Aufbau Principle:** In the ground state of the atoms, the orbitals are filled in order of their increasing energies

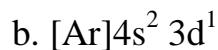
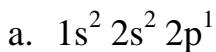
- **n+l rule**-Orbitals with lower value of (n+l) have lower energy. If two orbitals have the same value of (n+l) then orbital with lower value of n will have lower energy.
- The order in which the orbitals are filled is as follows:
1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d, 6p, 7s...
- **Pauli Exclusion Principle:** No two electrons in an atom can have the same set of four quantum numbers. Only two electrons may exist in the same orbital and these electrons must have opposite spin.
- **Hund's rule of maximum multiplicity:** Pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.
- **Electronic configuration of atoms:** Arrangement of electrons in different orbitals of an atom. The electronic configuration of different atoms can be represented in two ways.
 - $s^a p^b d^c \dots$ notation.
 - Orbital diagram: each orbital of the subshell is represented by a box and the electron is represented by an arrow (\uparrow) a positive spin or an arrow (\downarrow) a negative spin.
- **Stability of completely filled and half filled subshells:**
 - Symmetrical distribution of electrons- the completely filled or half filled sub-shells have symmetrical distribution of electrons in them and are more stable.
 - Exchange energy-The two or more electrons with the same spin present in the degenerate orbitals of a sub-shell can exchange their position and the energy released due to this exchange is called exchange energy. The number of exchanges is maximum when the subshell is either half filled or completely filled. As a result the exchange energy is maximum and so is the stability.

ONE MARK QUESTIONS

1. Neutrons can be found in all atomic nuclei except in one case. Which is this atomic nucleus and what does it consist of?
Ans. Hydrogen atom. It consists of only one proton.
2. Calculate wave number of yellow radiations having wavelength of 5800 \AA^0 .
Ans. Wave number = $1/\text{wavelength}$

$$\text{Wavelength} = 5800 \text{ \AA}^0 = 5800 \times 10^{-10} \text{ m}$$

$$\text{Wave number} = 1/5800 \times 10^{-10} \text{ m} = 1.72 \times 10^6 \text{ m}^{-1}$$
3. What are the values of n and l for 2p orbital?
Ans. n=2 and l= 1
4. Which of the following orbitals are not possible? 1p, 2s, 3f and 4d
Ans. 1p and 3f are not possible.
5. Write the electronic configuration of the element having atomic number 24.
Ans. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
6. What atoms are indicated by the following electronic configurations?



Ans. a. Boron b. Scandium

7. What is the relationship between frequency and wavelength of light?

Ans. velocity of light = frequency \times wavelength. Frequency and wavelength are inversely proportional to each other.

8. State Pauli Exclusion Principle.

Ans. No two electrons in an atom can have the same set of four quantum numbers or an orbital can have maximum two electrons and these must have opposite spin.

9. When α - rays hit a thin foil of gold, very few α - particles are deflected back.

What does it prove?

Ans. There is a very small heavy body present within the atom.

10. What is the difference between a quantum and a photon?

Ans. The smallest packet of energy of any radiation is called a quantum whereas that of light is called photon.

TWO MARKS QUESTIONS

1. Write the complete symbol for the atom with the given atomic number (Z) and mass number(A). (a) Z = 17, A = 35 (b) Z = 92, A = 233

Ans. (a) $^{35}_{17}\text{Cl}$ (b) $^{233}_{92}\text{U}$

2. Using s,p,d and f notation, describe the orbital with the following quantum numbers-

- (a) n=1, l=0 (b) n=3, l=1 (c) n=4, l=2 (d) n=4, l=3

Ans. (a) 1s (b) 3p (c) 4d (d) 4f

3. How many electrons in an atom have the following quantum numbers?

- a. n=4, $m_s = -1/2$ b. n = 3, l=0

Ans. (a) 16 electrons (b) 2 electrons.

4. An element with mass number 81 contains 31.7 % more neutrons as compared to protons. Assign the atomic symbol.

Ans. Mass number = 81, i.e., p + n = 81

$$\text{If protons} = x, \text{then neutrons} = x + \frac{31.7}{100} X x = 1.317 x$$

$$x + 1.317 x = 81 \text{ or } 2.317 x = 81$$

$$x = 35$$

Thus proton = 35, i.e., atomic no. = 35

Hence symbol is $^{81}_{35}\text{Br}$

5. (i) The energy associated with the first orbit in the hydrogen atom is $-2.18 \times 10^{-18} \text{ J/atom}$. What is the energy associated with the fifth orbit

(ii) Calculate the radius of Bohr's fifth orbit for hydrogen atom.

Ans. (i) $E_n = -2.18 \times 10^{-18} / n^2$ $E_5 = -2.18 \times 10^{-18} / 5^2 = -8.72 \times 10^{-20} \text{ J}$

(ii) For H atom, $r_n = 0.529 \times n^2$ $r_5 = 0.529 \times 5^2 = 13.225 \text{ Å} = 1.3225 \text{ nm}$

6. Explain, giving reasons, which of the following sets of quantum numbers are not possible.

- (a) n=0, l=0; $m_l = 0, m_s = +\frac{1}{2}$ (c) n=1, l=0; $m_l = 0, m_s = -\frac{1}{2}$

- (b) n=1, l=1; $m_l = -0, m_s = +\frac{1}{2}$ (d) n=2, l=1; $m_l = 0, m_s = +\frac{1}{2}$

Ans. (a) Not possible because $n \neq 0$ (c) Not possible because when $n=1, l \neq 1$

- (b) Possible (d) Possible
7. (a) What is the lowest value of n that allows g orbitals to exist?
 (b) An electron is in one of the $3d$ orbitals. Give the possible values of n, l and m_l for this electron.
- Ans. (a) minimum value of $n = 5$
 (b) $n=3, l=2, m_l = -2, -1, 0, +1, +2$
8. Calculate the total number of angular nodes and radial nodes present in 30 orbitals.
- Ans. For $3p$ orbitals, $n=3, l=1$
 Number of angular nodes = $l=1$
 Number of radial nodes = $n-l-1 = 3-1-1 = 1$
9. Mention the draw backs of Rutherford's atomic model.
 Ans. 1. It could not explain the stability of an atom.
 2. It could not explain the line spectrum of H^- atom.
10. State de-Broglie concept of dual nature of matter. How do dual nature of electron verified?

Ans. Just as light has dual nature, every material particle in motion has dual nature (particle nature and wave nature). The wave nature has been verified by Davisson and Germer's experiment whereas particle nature by scintillation experiment.

THREE MARKS QUESTIONS

1. State (a) Hund's Rule of maximum Multiplicity (b) Aufbau Principle (c) $n+l$ rule
- Ans.(a) Pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.
 (b) In the ground state of the atoms, the orbitals are filled in order of their increasing energies
 (c) Orbitals with lower value of $(n+l)$ have lower energy. If two orbitals have the same value of $(n+l)$ then orbital with lower value of n will have lower energy.

2. Write down the quantum numbers n and l for the following orbitals

- a. $2p$ b. $3d$ c. $5f$

Ans. a. $n=2, l=1$ b. $n=3, l=2$ c. $n=5, l=3$

3. Write the 3 points of difference between orbit and orbital.

Ans.

| Orbit | orbital |
|---|---|
| 1. An orbit is a well defined circular path around the nucleus in which the electrons revolve | 1. An orbital is the three dimensional space around the nucleus within which the probability of finding an electron is maximum(upto 90 %) |
| 2. It represents the planar motion of an electron around the nucleus | 2. It represents the three dimensional motion of an electron around the nucleus |
| 3. All orbits are circular and disc like | 3. Different orbitals have different shapes, i.e., s-orbitals are spherically symmetrical, p-orbitals are dumb-bell shaped and so on. |

4. State Heisenberg's uncertainty principle. calculate the uncertainty in the position of an electron if the uncertainty in its velocity is 5.7×10^5 m/s.

Ans. It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron. The product of their uncertainties is always equal to or greater than $h/4\pi$.

$$\Delta x \times (m \times \Delta v) = h/4\pi$$

$$\Delta x = h/4\pi \times m \times \Delta v = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 5.7 \times 10^5} = 1.0 \times 10^{-10} \text{ m}$$

5. Write 3 points of differences between electromagnetic waves and matterwaves.

| Electromagnetic waves | Matter waves |
|---|--|
| 1. These are associated with electric and magnetic fields | 1. These are not associated with electric and magnetic field. |
| 2. They do not require any medium for propagation. | 2. They require medium for propagation |
| 3. They travel with the same speed as that of light | 3. They travel with lower speeds not constant for all matter waves |

6. (i) Calculate the number of electrons which will together weigh one gram.
(ii) Calculate the mass and charge of one mole of electrons

Ans. (i) Mass of one electron = 9.10939×10^{-31} kg

$$\therefore \text{Number of electrons that weigh } 9.10939 \times 10^{-31} \text{ kg} = 1$$

$$\text{Number of electrons that will weigh 1 g} = (1 \times 10^{-3} \text{ kg})$$

$$= \frac{1}{9.10939 \times 10^{-31} \text{ kg}} \times (1 \times 10^{-3} \text{ kg})$$

$$= 0.1098 \times 10^{-3+31}$$

$$= 0.1098 \times 10^{28}$$

$$= 1.098 \times 10^{27}$$

$$(ii) \text{Mass of one electron} = 9.10939 \times 10^{-31} \text{ kg}$$

$$\text{Mass of one mole of electron} = (6.022 \times 10^{23}) \times (9.10939 \times 10^{-31} \text{ kg})$$

$$= 5.48 \times 10^{-7} \text{ kg}$$

Charge on one electron = 1.6022×10^{-19} coulomb

Charge on one mole of electron = $(1.6022 \times 10^{-19} \text{C}) (6.022 \times 10^{23})$

$$= 9.65 \times 10^4 \text{ C}$$

7. Find energy of each of the photons which
(i) correspond to light of frequency $3 \times 10^{15} \text{ Hz}$.
(ii) have wavelength of 0.50 \AA .

Ans.(i) Energy (E) of a photon is given by the expression,

$$E = h\nu$$

Where,

h = Planck's constant = $6.626 \times 10^{-34} \text{ Js}$ ν = frequency of light = $3 \times 10^{15} \text{ Hz}$

Substituting the values in the given expression of E :

$$E = (6.626 \times 10^{-34}) (3 \times 10^{15}) \quad E = 1.988 \times 10^{-18} \text{ J}$$

(ii) Energy (E) of a photon having wavelength (λ) is given by the expression,

$$E = \frac{hc}{\lambda}$$

h = Planck's constant = $6.626 \times 10^{-34} \text{ Js}$

c = velocity of light in vacuum = $3 \times 10^8 \text{ m/s}$

Substituting the values in the given expression of E :

$$E = \frac{(6.626 \times 10^{-34})(3 \times 10^8)}{0.50 \times 10^{-10}} = 3.976 \times 10^{-15} \text{ J}$$
$$\therefore E = 3.98 \times 10^{-15} \text{ J}$$

8. What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with $n = 4$ to an energy level with $n = 2$?

Ans. Then $i = 4$ to $f = 2$ transition will give rise to a spectral line of the Balmer series. The energy involved in the transition is given by the relation,

$$E = 2.18 \times 10^{-18} \left[\frac{1}{n_i^2} - \frac{1}{n_f^2} \right]$$

Substituting the values in the given expression of E :

$$E = 2.18 \times 10^{-18} \left[\frac{1}{4^2} - \frac{1}{2^2} \right]$$

$$= 2.18 \times 10^{-18} \left[\frac{1-4}{16} \right]$$

$$= 2.18 \times 10^{-18} \times \left(-\frac{3}{16} \right)$$

$$E = -(4.0875 \times 10^{-19} \text{ J})$$

The negative sign indicates the energy of emission.

Wavelength of light emitted $(\lambda) = \frac{hc}{E}$

$$\left(\text{since } E = \frac{hc}{\lambda} \right)$$

Substituting the values in the given expression of λ :

$$\lambda = \frac{(6.626 \times 10^{-34})(3 \times 10^8)}{4.0875 \times 10^{-19}}$$

$$\lambda = 4.8631 \times 10^{-7} \text{ m}$$

$$= 486.3 \times 10^{-9} \text{ m}$$

$$= 486 \text{ nm}$$

9. An atom of an element contains 29 electrons and 35 neutrons. Deduce (i) the number of protons and (ii) the electronic configuration of the element (iii) Identify the element .

Ans.(i)For an atom to be neutral, the number of protons is equal to the number of electrons.

\therefore Number of protons in the atom of the given element = 29

(ii) The electronic configuration of the atom is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$
 (iii) Copper

10. Give the number of electrons in the species H_2^+ , H_2 and O_2^+

Ans. Number of electrons present in hydrogen molecule (H_2) = $1 + 1 = 2$

\therefore Number of electrons in $H_2^+ = 2 - 1 = 1$

Number of electrons in $H_2 = 1 + 1 = 2$

Number of electrons present in oxygen molecule (O_2) = $8 + 8 = 16$

\therefore Number of electrons in $O_2^+ = 16 - 1 = 15$

FIVE MARKS QUESTIONS WITH ANSWERS

- What are the draw backs of Bohr's atomic model? Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the de Broglie wavelength associated with the electron revolving around the orbit.

Ans.1. Bohr's model failed to account for the finer details of the hydrogen spectrum.

- Bohr's model was also unable to explain spectrum of atoms containing more than one electron.
- Bohr's model was unable to explain Zeeman effect and Stark effect i
- Bohr's model could not explain the ability of atoms to form molecules by chemical bonds

Since a hydrogen atom has only one electron, according to Bohr's postulate, the angular momentum of that electron is given by:

$$mvr = n \frac{h}{2\pi} \dots\dots\dots(1)$$

Where, $n = 1, 2, 3, \dots$

According to de Broglie's equation:

$$\lambda = \frac{h}{mv}$$

$$\text{or } mv = \frac{h}{\lambda} \dots\dots\dots(2)$$

Substituting the value of ' mv ' from expression (2) in expression (1):

$$\frac{hr}{\lambda} = n \frac{h}{2\pi}$$

$$\text{or } 2\pi r = n\lambda \dots\dots\dots(3)$$

Since ' $2\pi r$ ' represents the circumference of the Bohr orbit (r), it is proved by equation (3) that the circumference of the Bohr orbit of the hydrogen atom is an integral multiple of de Broglie's wavelength associated with the electron revolving around the orbit.

- State photo electric effect. The work function for caesium atom is 1.9 eV. Calculate (a) the threshold wavelength and (b) the threshold frequency of the radiation. If the caesium element is irradiated with a wavelength 500 nm, calculate the kinetic energy and the velocity of the ejected photoelectron.

Ans. Photoelectric effect: The phenomenon of ejection of electrons from the surface of metal when light of suitable frequency strikes it is called photoelectric effect. The ejected electrons are called photoelectrons.

It is given that the work function (W_0) for caesium atom is 1.9 eV.

$$W_0 = \frac{hc}{\lambda_0}$$

(a) From the expression, $\lambda_0 = \frac{hc}{W_0}$, we get:

$$\lambda_0 = \frac{hc}{W_0}$$

Where,

λ_0 = threshold wavelength

h = Planck's constant

c = velocity of radiation

Substituting the values in the given expression of (λ_0):

$$\lambda_0 = \frac{(6.626 \times 10^{-34} \text{ Js})(3.0 \times 10^8 \text{ ms}^{-1})}{1.9 \times 1.602 \times 10^{-19} \text{ J}}$$

$$\lambda_0 = 6.53 \times 10^{-7} \text{ m}$$

Hence, the threshold wavelength λ_0 is 653 nm.

(b) From the expression, $W_0 = h\nu_0$, we get:

$$\nu_0 = \frac{W_0}{h}$$

Where,

ν_0 = threshold frequency

h = Planck's constant

Substituting the values in the given expression of ν_0 :

$$\nu_0 = \frac{1.9 \times 1.602 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ Js}}$$

$$(1 \text{ eV} = 1.602 \times 10^{-19} \text{ J})$$

$$\nu_0 = 4.593 \times 10^{14} \text{ s}^{-1}$$

Hence, the threshold frequency of radiation (ν_0) is $4.593 \times 10^{14} \text{ s}^{-1}$.

(c) According to the question:

Wavelength used in irradiation (λ) = 500 nm

Kinetic energy = $h(\nu - \nu_0)$

$$= hc \left(\frac{1}{\lambda} - \frac{1}{\lambda_0} \right)$$

$$= (6.626 \times 10^{-34} \text{ Js})(3.0 \times 10^8 \text{ ms}^{-1}) \left(\frac{\lambda_0 - \lambda}{\lambda \lambda_0} \right)$$

$$= (1.9878 \times 10^{-26} \text{ Jm}) \left[\frac{(653 - 500)10^{-9} \text{ m}}{(653)(500)10^{-18} \text{ m}^2} \right]$$

$$= \frac{(1.9878 \times 10^{-26})(153 \times 10^9)}{(653)(500)} \text{ J}$$

$$= 9.3149 \times 10^{-20} \text{ J}$$

Kinetic energy of the ejected photoelectron = $9.3149 \times 10^{-20} \text{ J}$

$$\text{Since K.E} = \frac{1}{2}mv^2 = 9.3149 \times 10^{-20} \text{ J}$$

$$v = \sqrt{\frac{2(9.3149 \times 10^{-20} \text{ J})}{9.10939 \times 10^{-31} \text{ kg}}}$$

$$= \sqrt{2.0451 \times 10^{11} \text{ m}^2 \text{s}^{-2}}$$

$$v = 4.52 \times 10^5 \text{ ms}^{-1}$$

Hence, the velocity of the ejected photoelectron (v) is $4.52 \times 10^5 \text{ ms}^{-1}$.

3. (a) The quantum numbers of six electrons are given below. Arrange them in order of increasing energies. If any of these combination(s) has/have the same energy lists:

1. $n=4, l=2, m_l=-2, m_s=-1/2$
2. $n=3, l=2, m_l=1, m_s=+1/2$
3. $n=4, l=1, m_l=0, m_s=+1/2$
4. $n=3, l=2, m_l=-2, m_s=-1/2$
5. $n=3, l=1, m_l=-1, m_s=+1/2$
6. $n=4, l=1, m_l=0, m_s=+1/2$

(b) Among the following pairs of orbitals which orbital will experience the larger effective nuclear charge? (i) $2s$ and $3s$, (ii) $4d$ and $4f$, (iii) $3d$ and $3p$

Ans.(a) For $n = 4$ and $l = 2$, the orbital occupied is $4d$.

For $n = 3$ and $l = 2$, the orbital occupied is $3d$.

For $n = 4$ and $l = 1$, the orbital occupied is $4p$.

Hence, the six electrons i.e., 1, 2, 3, 4, 5, and 6 are present in the $4d$, $3d$, $4p$, $3d$, $3p$, and $4p$ orbitals respectively.

Therefore, the increasing order of energies is $5(3p) < 2(3d) = 4(3d) < 3(4p) = 6(4p) < 1(4d)$.

(b) Nuclear charge is defined as the net positive charge experienced by an electron in the orbital of a multi-electron atom. The closer the orbital, the greater is the nuclear charge experienced by the electron (s) in it.

(i) The electron(s) present in the $2s$ orbital will experience greater nuclear charge (being closer to the nucleus) than the electron(s) in the $3s$ orbital.

(ii) $4d$ will experience greater nuclear charge than $4f$ since $4d$ is closer to the nucleus.

(iii) $3p$ will experience greater nuclear charge since it is closer to the nucleus than $3f$.

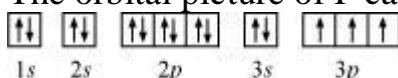
4. (i) The unpaired electrons in Al and Si are present in $3p$ orbital. Which electrons will experience more effective nuclear charge from the nucleus?
 - (ii) Indicate the number of unpaired electrons in: (a) P, (b) Si, (c) Cr, (d) Fe
- Ans. (i) the electrons in the $3p$ orbital of silicon will experience a more effective nuclear charge than aluminium.

(ii) (a) Phosphorus (P):

Atomic number = 15

The electronic configuration of P is: $1s^2 2s^2 2p^6 3s^2 3p^3$

The orbital picture of P can be represented as:



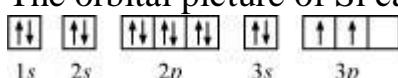
From the orbital picture, phosphorus has **three** unpaired electrons.

(b) Silicon (Si):

Atomic number = 14

The electronic configuration of Si is: $1s^2 2s^2 2p^6 3s^2 3p^2$

The orbital picture of Si can be represented as:



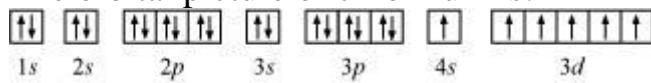
From the orbital picture, silicon has **two** unpaired electrons.

(c) Chromium (Cr):

Atomic number = 24

The electronic configuration of Cr is: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

The orbital picture of chromium is:



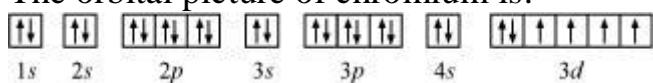
From the orbital picture, chromium has **six** unpaired electrons.

(d) Iron (Fe):

Atomic number = 26

The electronic configuration is: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

The orbital picture of chromium is:



From the orbital picture, iron has **four** unpaired electrons.

HOTS QUESTIONS WITH ANSWERS

- Give the name and atomic number of the inert gas atom in which the total number of d-electrons is equal to the difference between the numbers of total p and total s electrons.

Ans. electronic configuration of Kr (atomic no.=36) = $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

Total no. of s-electrons = 8, total no. of p-electrons = 18. Difference = 10

No. of d- electrons = 10

- What is the minimum product of uncertainty in position and momentum of an electron?

Ans. $h/4\pi$

- Which orbital is non-directional ?

Ans. s- orbital

- What is the difference between the notations l and L ?

Ans. l represents the sub-shell and L represent shell.

- How many electrons in an atom can have $n + l = 6$?

Ans. 18

- An anion A³⁺ has 18 electrons. Write the atomic number of A.

Ans. 15

- Arrange the electron (e), protons (p) and alpha particle (α) in the increasing order for the values of e/m (charge/mass).

Ans., $\alpha < p < e$

CHAPTER-3

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES OF ELEMENTS

Mandeleev's Periodic Law:- The properties of the elements are the periodic function of their atomic masses.

Moseley, the English physicist showed that atomic number is more fundamental property of an element than its atomic mass. Therefore, the position of an element in the periodic table depends on its atomic number than its atomic mass.

Modern Periodic Law: The physical and chemical properties of elements are the periodic functions of their atomic numbers.

Types of Elements: s-, p-, d- and f- blocks.

MAIN GROUP ELEMENTS/ REPRESENTATIVE ELEMENTS:

The s- and p- block elements are called main group elements or representative elements.

s- block elements: Group-1 (Alkali metals) and Group-2 elements (Alkaline earth metals) which respectively have ns^1 and ns^2 outermost electronic configurations.

p- Block elements: They belongs to group- 13 to 18. The outer most electronic configuration is $ns^2 np^{1-6}$. He ($1s^2$) is a s- block element but is positioned with the group 18 elements ($ns^2 np^6$) because it has completely filled valence shell and as a result, exhibits properties characteristic of other noble gases.

d- block elements (Transition elements) are the elements of group 3 to 12 having outer electronic configuration $(n-1)d^{1-10} ns^{1-2}$. Four transition series are 3d, 4d, 5d and 6d. The 6d- series is incomplete. Atomic radius generally decreases across a period and increases as we descend the group.

f-Block elements (Inner- transition Series)

Lanthanoids characterised by the filling of 4 f-orbitals, are the elements following lanthanum from $_{58}\text{Ce}$ to $_{71}\text{Lu}$. Actinoids characterised by filling of 5f-orbitals, are the elements following actinium from $_{70}^{\text{Th}}$ to $_{103}\text{Lr}$. Characteristic outer electronic configuration is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$.

Noble Gases: The gaseous elements of group 18 are called noble gases. The general outermost electronic configuration of noble gases (except He) is $ns^2 np^6$. He exceptionally has $1s^2$ configuration. Thus the outermost shell of noble gases is completely filled.

PERIODICITY: The repetition of similar properties after regular intervals is called periodicity.

Cause of Periodicity: The properties of elements are the periodic repetition of similar electronic configuration of elements as the atomic number increases.

ATOMIC PROPERTIES: The physical characteristics of the atom of an element are called atomic properties. The properties such as atomic radius, ionic radius, ionisation energy, electro-negativity, electron affinity and valence etc., called atomic properties.

ATOMIC RADIUS- The distance from the centre of the nucleus to the outermost shell of the electrons in the atom of any element is called its atomic radius.

Periodicity- (a) In period- Atomic radius of elements decreases from left to right in a period.

(b) In Group- Atomic radius of elements increases on moving top to bottom in a group.

COVALENT RADIUS- Half the inter-nuclear distance between two similar atoms of any element which are covalently bonded to each other by a single covalent bond is called covalent radius.

VAN DER WAALS' RADIUS: Half the inter-nuclear separation between two similar adjacent atoms belonging to the two neighbouring molecules of the same substance in the solid state is called the van der waals'radius of that atom.

METALLIC RADIUS: Half the distance between the nuclei of the two adjacent metal atoms in a close packed lattice of the metal is called its metallic radius.

Van der Waals'radius > Metallic radius > Covalent radius

IONIC RADIUS: The effective distance from the centre of the nucleus of an ion upto which it has an influence on its electron cloud is called its ionic radius.

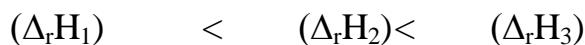
A cation is smaller but the anion is larger than the parent atom. In case of iso-electronic species, the cation with greater positive charge has smaller radius but anion with greater negative charge has the larger radii.

IONISATION ENTHALPY: The ionisation enthalpy is the molar enthalpy change accompanying the removal of an electron from a gaseous phase atom or ion in its ground state. Thus enthalpy change for the reaction; $M_{(g)} \rightarrow M^+_{(g)} + e^-$

Is the ionisation enthalpy of the element M. Like ionisation energies for successive ionisation, the successive ionisation enthalpy may also be termed as 2nd ionisation enthalpy ($\Delta_r H_2$), third ionisation enthalpy ($\Delta_r H_3$) etc. The term ionisation enthalpy is taken for the first ionisation enthalpy, ($\Delta_r H_1$) is expressed in kg mol⁻¹ or in eV.

Periodicity:

- i) Generally the ionisation enthalpies follow the order (there are few exceptions):

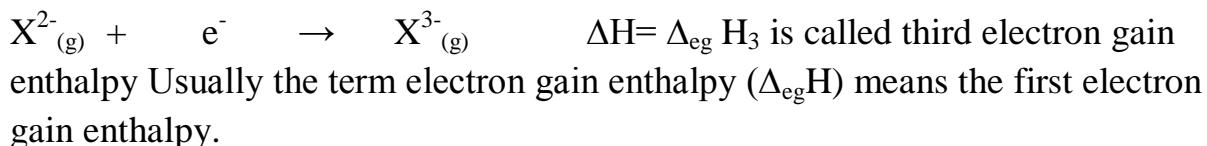
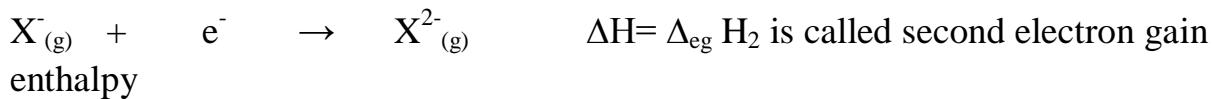


- ii) The ionisation enthalpy decreases on moving top to bottom in a group.
- iii) The ionisation enthalpy increases on moving from left to right in a period.

ELECTRON GAIN ENTHALPY: The electron gain enthalpy (($\Delta_{eg} H$) is the molar enthalpy change when an isolated gaseous atom or ion in its ground state adds an electron to form the corresponding anion thus the enthalpy change for the reaction; $X_{(g)} + e^- \rightarrow X^-_{(g)}$

Is called the electron gain enthalpy ($\Delta_{eg} H$) of the element X. The $\Delta_{eg} H$ may be positive or negative.

The successive values for the addition of second, third etc. Electron, these are called second, third etc. electron gain enthalpies. For example,



Periodicity:

- (i) In period- The electron gain enthalpy increases from left to right in a period.
- (ii) In group- The electron gain enthalpy decreases from top to bottom in a group.

ELECTRONEGATIVITY: “The relative tendency of an atom in a molecule to attract the shared pair of electrons towards itself is termed as its electronegativity.”

Periodicity:

- (i) In period- The electro-negativity increases from left to right in a period.
- (ii) In group- The electro-negativity decreases from top to bottom in a group.

VALENCE ELECTRONS: The electrons present in outermost shell are called as valence electron. Because the electrons in the outermost shell determine the valency of an element.

VALENCY OF AN ELEMENT: The number of hydrogen or halogen atom or double the number of oxygen atom, which combine with one atom of the element is taken as its valency. According to the electronic concept of valency, “the number of electrons which an atom loses or gains or shares with other atom to attain the noble gas configuration is termed as its valency.”

Periodicity:

- (i) In period- The valency first increases then decreases from left to right in a period.
- (ii) In group- The valency remains constant from top to bottom in a group.

ELECTROPOSITIVE OR METALLIC CHARACTER: The tendency of an element to lose electrons and forms positive ions (cations) is called electropositive or metallic character. The elements having lower ionisation energies have higher tendency to lose electrons, thus they are electropositive or metallic in their behaviour.

Alkali metals are the most highly electropositive elements.

Periodicity: In period- The electropositive or metallic characters decreases from left to right in a period.

In group- The electropositive or metallic characters increases from top to bottom in a group.

ELECTRO-NEGATIVE OR NON- METALLIC CHARACTERS: the tendency of an element to accept electrons to form an anion is called its non metallic or electronegative character. The elements having high electro-negativity have higher tendency to gain electrons and forms anion. So, the elements in the upper right hand portion of the periodic table are electro-negative or non-metallic in nature.

Periodicity:

- (i) In period- The electro-negative or non- metallic characters increases from left to right in a period.
- (ii) In group- The electro-negative or non-metallic characters decreases from top to bottom in a group.

REACTIVITY OF METALS:

Periodicity:

- (i) In period- The tendency of an element to lose electrons decreases in a period. So the reactivity of metals decreases from left to right in a period.
- (ii) In group- The tendency of an element to lose electrons increases in a period. So the reactivity of metals increases from top to bottom in a group.

REACTIVITY OF NON- METALS:

- (i) In period- The tendency of an element to gain electrons increases in a period. So the reactivity of non-metals increases from left to right in a period.
- (ii) In group- The tendency of an element to gain electrons decreases in a group. So the reactivity of non-metals increases from top to bottom in a group.

SOLUBILITY OF ALKALI METALS CARBONATES AND BICARBONATES:

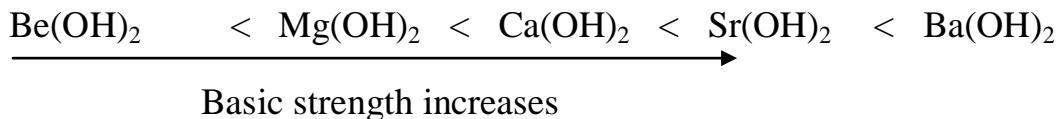
PERIODICITY IN GROUP: The solubility of alkali metal carbonates and bicarbonates in water increases down the group (From Lithium to Caesium).

SOLUBILITY OF ALKALINE EARTH METAL HYDROXIDES AND SULPHATES:

PERIODICITY IN GROUP: The solubility of alkaline earth metal hydroxide and sulphates in water increases down the group (From Beryllium to Barium).

BASIC STRENGTH OF ALKALINE EARTH METAL HYDROXIDES:

PERIODICITY IN GROUP: The basic strength of alkaline earth metal hydroxide in water increases down the group (From Beryllium to Barium), i.e.,



THERMAL STABILITY OF CARBONATES OF ALKALI AND ALKALINE EARTH METALS:

Except lithium carbonate, (LiCO_3), the carbonates of all other alkali metals are stable towards heat, i.e., carbonates of alkali metals (except LiCO_3) do not decompose on heating. LiCO_3 decomposes on heating to give lithium oxide (LiCO_3).

The carbonates of alkaline earth metals are relatively less stable. On heating, they decompose to give corresponding oxide and CO_2 gas. The decomposition temperature for alkaline earth metal carbonates increases as we go down the group.

Anomalous Properties of Second Period Elements

Their anomalous behaviour is attributed to their small size, large charge/radius ratio, high electro negativity, non- availability of d- orbitals in their valence shell. the first member of each group of p-Block elements displays greater ability to form pp-pp multiple bonds to itself (e.g. $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$ $\text{O}=\text{O}$, $\text{N}\equiv\text{N}$) and to other second period elements (e.g. $\text{C}=\text{O}$, $\text{C}\equiv\text{N}$, $\text{N}=\text{O}$) compared to subsequent member of the group.

ONE MARK QUESTIONS

Q1. Select the species which are iso-electronic (same number of electron) with each other.

- (1) Ne (2) Cl^- (3) Ca^{2+} (4) Rb^+

Ans-The Cl^- and Ca^{2+} . Both have 18 e⁻ each.

Q.2. What the elements of a group have common among them?

Ans- They have same number of electrons in the valence shell.

Q.3. What the s- and p- block elements are collectively called?

Ans- Representative elements.

Q.4. Define atomic radius.

Ans- The one-half the distance between the nuclei of two covalently bonded atoms of the same element in a molecule is called as atomic radius.

Q.5. State the modern periodic law.

Ans- The physical and chemical properties of the elements are the periodic function of their atomic numbers.

Q.6. Name the groups of elements classified as s-, p- and d- blocks.

Ans- s- block= 1,2 (including He), p- block= 13 to 18 (except He), d- block= 3 to 12.

Q.7. Define the term ionisation enthalpy.

Ans- The energy required to remove the outer most electron from the valence shell of an isolated gaseous atom is called as ionisation enthalpy.

Q.8. In how many groups and periods the elements in modern periodic table are classified?

Ans- In 18 groups and 7 periods.

Q.9. What do you mean by electronic configuration of the elements?

Ans- The systematic distribution of the electrons among the orbitals of an atom of an element according to increasing order of their energies is called as electronic configuration of that element.

TWO MARKS QUESTIONS

Q.1. Describe the two merits of long form periodic table over the Mendeleev's periodic table?

Ans- 1. It removed the anomalies about the position of isotopes which existed in the Mendeleev's table.

2. It relates the position of an element in the periodic table with its electronic configuration.

Q.2. What is a period in the periodic table? How do atomic sizes change in a period with an increase in atomic number?

Ans- The horizontal rows in periodic table are called as periods. The atomic sizes decrease in a period with an increase in atomic number.

Q.3. The outer electronic configuration of some elements are:

- (a) $3s^2 3p^4$ (b) $3d^{10} 4s^2$ (c) $3s^2 3p^6 4s^2$ (d) $6s^2 4f^3$

To which block of elements in the periodic table each of these belongs?

Ans- (a) p- Block (b) d- Block (c) s- Block (d) f- Block

Q.4. What is meant by periodicity in properties of elements? What is the reason behind this?

Ans- The repetition of similar properties after regular intervals is called as periodicity. It is due to the similarity in the outer electronic configurations which gives rise to the periodic properties of the elements.

Q.5. How do atomic radii vary in a group and a period?

Ans- In group- Atomic size increases on moving from top to bottom.

In period- Atomic size decreases on moving left to right in a period.

Q.6. Arrange the following in the order of increasing radii:

- (a) I, I^+ , I^- (b) F, Cl, Br

Ans- (a) $I^+ < I < I^-$ (b) O < N < P

Q.7. Name the factors which affect the ionisation enthalpy of an element.

Ans- (i) Size of atom or ion (ii) Nuclear charge (iii) Electronic configuration

 (iv) Screening effect (v) Penetration effect of the electrons

Q.8. How does ionisation enthalpy vary in a group and a period?

Ans- In Period- It increases from left to right

In group- It decreases down the group.

Q.9. Noble gases have zero electron gain enthalpy values. Explain.

Ans- Because the outer most shell of noble gases is completely filled and no more electrons can be added.

Q.10. Elements in the same group have equal valency. Comment on it.

Ans- Because the general outer most electronic configurations of the elements of a group remain same and they contain equal number of electrons in their respective outer most shells.

THREE MARKS QUESTIONS

Q.1. The first ionisation enthalpy of magnesium is higher than that of sodium. On the other hand, the second ionisation enthalpy of sodium is very much higher than that of magnesium. Explain.

Ans- The 1st ionisation enthalpy of magnesium is higher than that of Na due to higher nuclear charge and slightly smaller atomic radius of Mg than Na. After the loss of first electron, Na^+ formed has the electronic configuration of neon (2,8). The higher stability of the completely filled noble gas configuration leads to very high second ionisation enthalpy for sodium. On the other hand, Mg^+ formed after losing first electron still has one more electron in its outermost (3s) orbital. As a result, the second ionisation enthalpy of magnesium is much smaller than that of sodium.

Q.2. What are the major differences between metals and non-metals?

Ans-

| Property | Metal | Non-Metal |
|---------------------|---------------------------------|----------------------------|
| Nature | Electropositive | Electronegative |
| Type of ion formed | Cation (Positively Charged) | Anion (Negatively Charged) |
| Reaction with acids | Active metals displace hydrogen | Do not displace hydrogen |
| Oxides | Basic | Acidic |

Q.3. Among the elements of the second period Li to Ne pick out the element:

- (i) with the highest first ionisation energy
- (ii) with the highest electronegativity
- (iii) with the largest atomic radius Give the reason for your choice.

Ans- (i) The ionisation energy increases on going from left to right. Therefore, the element with the highest ionisation energy is Ne.

(ii) The electro negativity is electron- accepting tendency. This increases on going from left to right and decreases down the group. Therefore, the element with the highest electro- negativity is F.

(iii) The atomic radius decreases across a period on going from left to right. Thus, the first element of any period should have the largest atomic radii. Here, Li has the largest atomic radii.

Q.4. Arrange the following as stated:

- (i) N₂, O₂, F₂, Cl₂ (Increasing order of bond dissociation energy)
- (ii) F, Cl, Br, I (Increasing order of electron gain enthalpy)
- (iii) F₂, N₂, Cl₂, O₂ (Increasing order of bond length)

Ans- (i) F₂ < Cl₂ < O₂ < N₂
(ii) I < Br < F < Cl
(iii) N₂ < O₂ < F₂ < Cl₂

Q.5. Why does the first ionisation enthalpy increase as we go from left to right through a given period of the periodic table?

Ans- In a period, the nuclear charge (the number of protons) increases on going from left to right. The electron added to each element from left to right enters the same shell. This results in an increase of the effective nuclear charge across the period on moving from left to right. As a result, the electron get more firmly bound to the nucleus. This causes an increase in the first ionisation enthalpy across the period.

Q.6. Use the periodic table to answer the following questions.

- (i) Identify the element with five electrons in the outer sub-shell.
- (ii) Identify an element that would tend to lose two electrons.
- (iii) Identify an element that would tend to gain two electrons.

Ans- (i) Chlorine (ii) Magnesium (iii) Oxygen

Q.7. Explain why are cations smaller and anions larger in size than their parent atoms?

Ans- (a) The cations are smaller than their parent atoms due to the following reasons:

- (i) Disappearance of the valence shell.
- (ii) Increase of effective nuclear charge

(b) The anions are larger than their parent atoms due to the following reason:

An increase in the number of electrons in the valence shell reduces the effective nuclear charge due to greater mutual shielding by the electrons. As a result, electron cloud expands, i.e., the ionic radius increases.

Q.8. Describe the theory associated with the radius of an atom as it

- (a) gains an electron (b) loses an electron

Ans- (a) When an atom gains an electron, its size increases. When an electron is added, the number of electrons goes up by one. This results in an increase in repulsion among the electrons. However, the number of protons remains the same. As a result, the effective nuclear charge of the atom decreases and the radius of the atom increases.

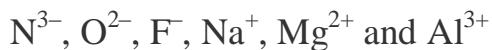
(b) When an atom loses an electron, the number of electrons decreases by one while the nuclear charge remains the same. Therefore, the interelectronic repulsions in the atom decrease. As a result, the effective nuclear charge increases. Hence, the radius of the atom decreases.

Q.9. How does atomic radius vary in a period and in a group? How do you explain the variation?

Ans- Atomic radius generally decreases from left to right across a period. This is because within a period, the outer electrons are present in the same valence shell and the atomic number increases from left to right across a period, resulting in an increased effective nuclear charge. As a result, the attraction of electrons to the nucleus increases.

On the other hand, the atomic radius generally increases down a group. This is because down a group, the principal quantum number (n) increases which results in an increase of the distance between the nucleus and valence electrons.

Q.10. Consider the following species:



- (a) What is common in them?
- (b) Arrange them in the order of increasing ionic radii.

Ans- (a) the same number of electrons (10 electrons). Hence, the given species are isoelectronic.



FIVE MARKS QUESTIONS

Q.1. What is the cause of the periodicity in the properties of the elements? How do the following properties vary in (a) a group and (b) in a period

- (i) electronegativity (ii) ionisation enthalpy (iii) Atomic size

Ans- It is due to the similarity in the outer electronic configurations which gives rise to the periodic properties of the elements.

(a) In a group:

- (i) Electronegativity- It decreases down the group.
(ii) Ionisation enthalpy- It decreases down the group.
(iii) Atomic size- It increases down the group.

(b) In a period:

- (i) Electronegativity- Increases
(ii) Ionisation enthalpy- Increases
(iii) Atomic size- Decreases.

Q.2. The first (Δ_iH_1) and the second (Δ_iH) ionization enthalpies (in kJ mol^{-1}) and the ($\Delta_{eg}H$) electron gain enthalpy (in kJ mol^{-1}) of a few elements are given below:

| Elements | Δ_iH_1 | Δ_iH | $\Delta_{eg}H$ |
|----------|---------------|-------------|----------------|
| I | 520 | 7300 | -60 |
| II | 419 | 3051 | -48 |
| III | 1681 | 3374 | -328 |
| IV | 1008 | 1846 | -295 |
| V | 2372 | 5251 | +48 |
| VI | 738 | 1451 | -40 |

Which of the above elements is likely to be :

- (a) the least reactive element. (b) the most reactive metal.
- (c) the most reactive non-metal. (d) the least reactive non-metal.
- (e) the metal which can form a stable binary halide of the formula MX_2 , ($\text{X}=\text{halogen}$).
- (f) the metal which can form a predominantly stable covalent halide of the formula MX ($\text{X}=\text{halogen}$)?

Ans- (a) Element V is likely to be the least reactive element. This is because it has the highest first ionization enthalpy ($\Delta_i\text{H}_1$) and a positive electron gain enthalpy ($\Delta_{eg}\text{H}$).

- (b) Element II is likely to be the most reactive metal as it has the lowest first ionization enthalpy ($\Delta_i\text{H}_1$) and a low negative electron gain enthalpy ($\Delta_{eg}\text{H}$).
- (c) Element III is likely to be the most reactive non-metal as it has a high first ionization enthalpy ($\Delta_i\text{H}_1$) and the highest negative electron gain enthalpy ($\Delta_{eg}\text{H}$).
- (d) Element V is likely to be the least reactive non-metal since it has a very high first ionization enthalpy ($\Delta_i\text{H}_2$) and a positive electron gain enthalpy ($\Delta_{eg}\text{H}$).
- (e) Element VI has a low negative electron gain enthalpy ($\Delta_{eg}\text{H}$). Thus, it is a metal. Further, it has the lowest second ionization enthalpy ($\Delta_i\text{H}_2$). Hence, it can form a stable binary halide of the formula MX_2 ($\text{X}=\text{halogen}$).
- (f) Element I has low first ionization energy and high second ionization energy. Therefore, it can form a predominantly stable covalent halide of the formula MX ($\text{X}=\text{halogen}$).

CHAPTER-4

CHEMICAL BONDING AND MOLECULAR STRUCTURE

OCTET RULE- During a chemical reaction the atoms tend to adjust their electronic arrangement in such a way that they achieve $8 e^-$ in their outermost electron. This is called octet rule.

CHEMICAL BOND- the chemical force which keeps the atoms in any molecule together is called a chemical bond.

IONIC BOND- The columbic force of attraction which holds the appositively charged ions together is called an ionic bond. An ionic bond is formed by the complete transfer of one or more electrons from the atom of a metal to an atom of non-metal.

LATTICE ENTHALPY- The molar enthalpy change accompanying the complete separation of the constituent particles that compose of the solids (such as ions for ionic solid, molecules for molecular solids) under standard conditions is called lattice enthalpy ($\Delta_l H^\circ$). The lattice enthalpy is a positive quantity.

ELECTRO VALENCY: The number of electrons lost or gain by an atom of an element is called as electrovalency.

The element which give up electrons to form positive ions are said to have positive valency, while the elements which accept electrons to form negative ions are said to have negative valency.

FORMATION OF AN IONIC BOND: It is favoured by, (i) the low ionisation enthalpy of a metallic element which forms the cations, (ii) High electron gain enthalpy of non-metallic element which forms the anions, (iii) Large lattice enthalpy i.e; the smaller size and the higher charge of the atoms.

COVALENCY: The number of electrons which an atom contributes towards mutual sharing during the formation of a chemical bond called its covalency in that compound.

SINGLE COVALENT BOND: A covalent bond formed by the mutual sharing of one pair of electrons is called a single covalent bond, or simply a single bond. A single covalent bond is represented by a small line (—) between the two atoms.

DOUBLE COVALENT BOND: A covalent bond formed by the mutual sharing of two pair of electrons is called a double covalent bond, or simply a double bond. A double covalent bond is represented by two small horizontal lines (=) between the two atoms. E.g. O=O, O=C=O etc.

TRIPLE COVALENT BOND: A covalent bond formed by the mutual sharing of three pair of electrons is called a triple covalent bond, or simply a triple bond. A triple covalent bond is represented by three small horizontal lines (\equiv) between the two atoms. E.g. N≡N, H-C≡C-H etc.

FORMATION OF A COVALENT BOND: Formation of a covalent bond is favoured by

- (i) High ionisation enthalpy of the combining elements.
- (ii) Nearly equal electron gain enthalpy and equal electro-negativities of combining elements.
- (iii) High nuclear charge and small atomic size of the combining elements.

POLAR COVALENT BOND: The bond between two unlike atoms which differ in their affinities for electrons is said to be polar covalent bond. E.g. H-Cl

COORDINATE BOND: The bond formed when one sided sharing of electrons take place is called a coordinate bond. Such a bond is also known as dative bond. It is represented by an arrow (\rightarrow) pointing towards the acceptor atom. E.g. $\text{H}_3\text{N} \rightarrow \text{BF}_3$

Bond Length: Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule

Bond Angle: It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion

Bond Enthalpy: It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state.

Bond Order: In the Lewis description of covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule

Resonance: whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately

Dipole moment : The product of the magnitude of the charge and the distance between the centres of positive and negative charge. It is a vector quantity and is represented by an arrow with its tail at the positive centre and head pointing towards a negative centre. Dipole moment (μ) = charge (Q) \times distance of separation (r)

SIGMA BOND: A covalent bond formed due to the overlapping of orbitals of the two atoms along the line joining the two nuclei (orbital axis) is called sigma (σ) bond. For example, the bond formed due to s-s and s-p, p-p overlapping along the orbital axis are sigma bonds.

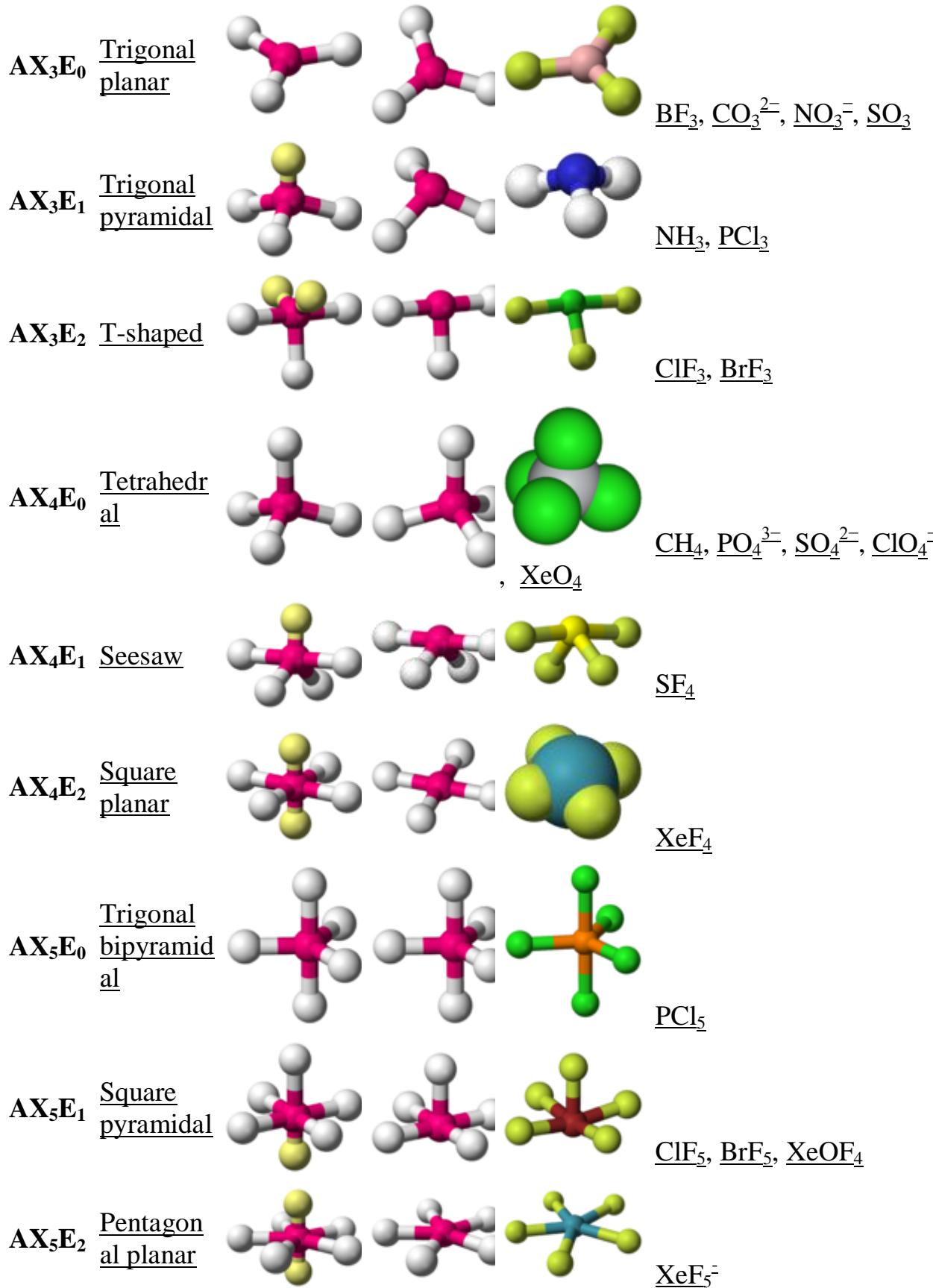
Pi- BOND: A covalent bond formed by the side wise overlapping of p- or d- orbitals of two atoms is called as pi (π) bond. For example, the bond formed due to the sideways overlapping of the two p- orbitals is a pi- bond.

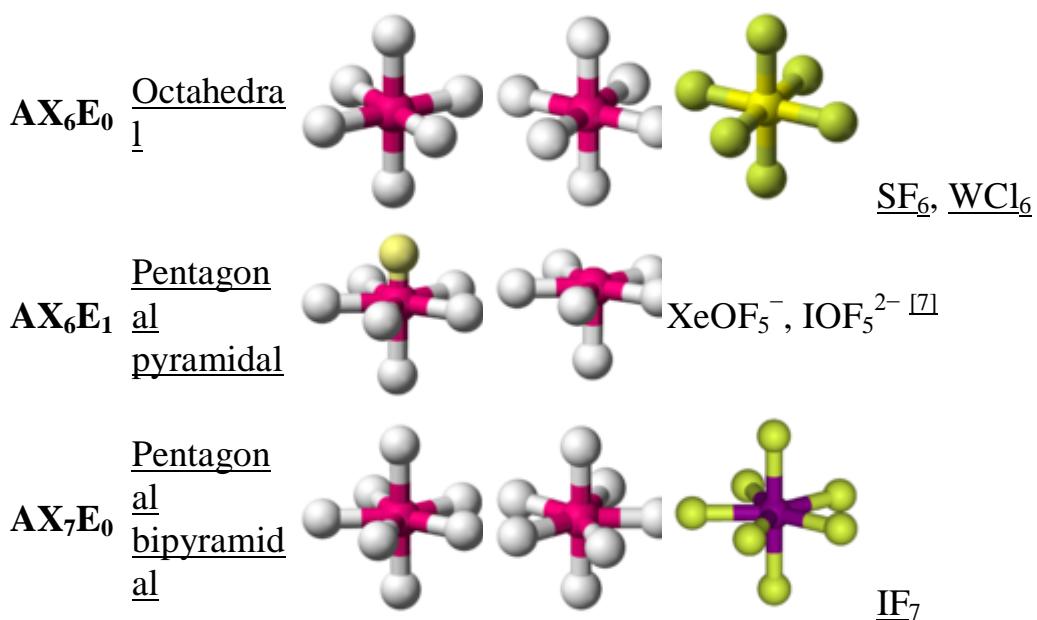
HYDROGEN BOND: The bond between the hydrogen atom of one molecule and a more electro- negative element of same or another molecule is called as hydrogen bond.

HYBRIDIZATION: The process of mixing of the atomic orbitals to form new hybrid orbitals is called hybridization. All hybrid orbitals of a particular kind have equal energy, identical shapes and are symmetrically oriented in shape.

The hybrid orbitals are designed according to the type and the atomic orbitals merging together, e.g.,

| Molecule Type | Shape | Electron arrangement [†] | Geometry [‡] | Examples |
|---------------------------------------|-------|-----------------------------------|-----------------------|---|
| AX_2E_0 <u>Linear</u> | | | | <u>BeCl₂</u> , <u>HgCl₂</u> , <u>CO₂</u> |
| AX_2E_1 <u>Bent</u> | | | | <u>NO₂⁻</u> , <u>SO₂</u> , <u>O₃</u> , <u>CCl₂</u> |
| AX_2E_2 <u>Bent</u> | | | | <u>H₂O</u> , <u>OF₂</u> |
| AX_2E_3 <u>Linear</u> | | | | <u>XeF₂</u> , <u>I₃⁻</u> , <u>XeCl₂</u> |





ONE MARK QUESTIONS

Q.1. What is the total number of sigma and pi bonds in the following molecules?

- (a) C₂H₂ (b) C₂H₄

Ans- there are three sigma and two pi-bonds in C₂H₂.

there are five sigma bonds and one pi-bond in C₂H₄.

Q.2. Write the significance of a plus and a minus sign shown in representing the orbitals.

Ans- Molecular orbitals are represented by wave functions. A plus sign in an orbital indicates a positive wave function while a minus sign in an orbital represents a negative wave function.

Q.3. How do you express the bond strength in terms of bond order?

Ans- Bond strength represents the extent of bonding between two atoms forming a molecule. The larger the bond energy, the stronger is the bond and the greater is the bond order.

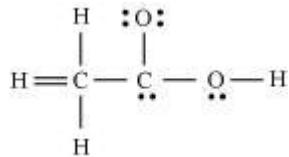
Q.5. Define the bond length.

Ans- Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule.

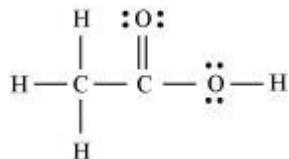
Q.6. Arrange the bonds in order of increasing ionic character in the molecules: LiF, K₂O, N₂, SO₂ and ClF₃.

Ans- N₂ < SO₂ < ClF₃ < K₂O < LiF.

Q.7. The skeletal structure of CH₃COOH as shown below is correct, but some of the bonds are shown incorrectly. Write the correct Lewis structure for acetic acid.



Ans- The correct Lewis structure for acetic acid is as follows:



Q.8. Define octet rule.

Ans- The elements tend to adjust the arrangement of their electrons in such a way that they (except H and He) achieve eight electrons in their outermost shell. This is called octet rule.

Q.9. Define lattice enthalpy.

Ans- The energy required when one mole of an ionic compound in crystalline form is split into the constituent ions is called lattice enthalpy.

Q.10. Which type of bond is formed when the atoms have zero difference in electronegativity?

Ans- Covalent bond.

TWO MARKS QUESTIONS

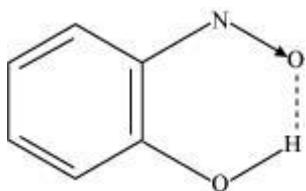
Q.1. Define hydrogen bond. Is it weaker or stronger than the van der Waals forces?

Ans- A hydrogen bond is defined as an attractive force acting between the hydrogen attached to an electronegative atom of one molecule and an electronegative atom of a different molecule (may be of the same kind).

There are two types of H-bonds:

(i) Intermolecular H-bond e.g., HF, H₂O etc.

(ii) Intramolecular H-bond e.g., o-nitrophenol



Hydrogen bonds are stronger than Van der Walls forces since hydrogen bonds are regarded as an extreme form of dipole-dipole interaction.

Q.2. Write the favourable factors for the formation of ionic bond.

Ans-(i) Low ionization enthalpy of metal atom.

(ii) High electron gain enthalpy ($\Delta_{eg} H$) of a non-metal atom.

(iii) High lattice energy of the compound formed.

Q.3. Although geometries of NH₃ and H₂O molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. Discuss.

Ans- The molecular geometry of NH₃ and H₂O can be shown as:



The central atom (N) in NH₃ has one lone pair and there are three bond pairs. In H₂O, there are two lone pairs and two bond pairs.

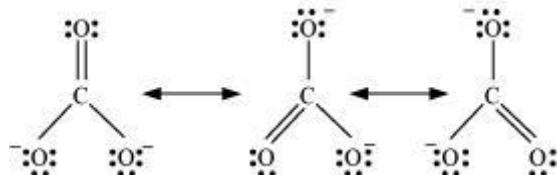
The two lone pairs present in the oxygen atom of H₂O molecule repels the two bond pairs. This repulsion is stronger than the repulsion between the lone pair and the three bond pairs on the nitrogen atom.

Since the repulsions on the bond pairs in H₂O molecule are greater than that in NH₃, the bond angle in water is less than that of ammonia.

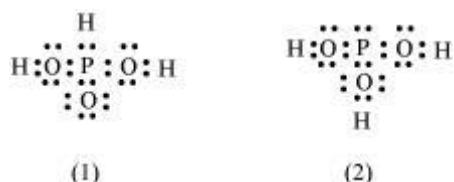
Q.4. Explain the important aspects of resonance with reference to the CO₃²⁻ ion.

Ans- According to experimental findings, all carbon to oxygen bonds in CO_3^{2-} are equivalent. Hence, it is inadequate to represent CO_3^{2-} ion by a single Lewis structure having two single bonds and one double bond.

Therefore, carbonate ion is described as a resonance hybrid of the following structures:



Q.5. H_3PO_3 can be represented by structures 1 and 2 shown below. Can these two structures be taken as the canonical forms of the resonance hybrid representing H_3PO_3 ? If not, give reasons for the same.



Ans- The given structures cannot be taken as the canonical forms of the resonance hybrid of H_3PO_3 because the positions of the atoms have changed.

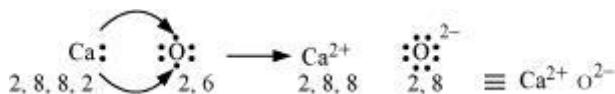
Q.6. Use Lewis symbols to show electron transfer between the following atoms to form cations and anions: (a) Ca and O (c) Al and N.

Ans(a) Ca and O:

The electronic configurations of Ca and O are as follows:

Ca: 2, 8, 8, 2 O: 2, 6

Oxygen requires two electrons more to complete its octet, whereas calcium has two electrons more than the nearest noble gas i.e., Argon. Hence, the electron transfer takes place as:

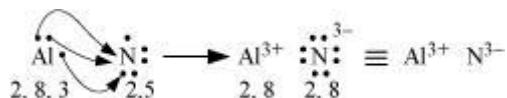


(b) Al and N:

The electronic configurations of Al and N are as follows:

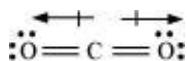
Al: 2, 8, 3 N: 2, 5

Nitrogen is three electrons short of the nearest noble gas (Neon), whereas aluminium has three electrons more than Neon. Hence, the electron transference can be shown as:



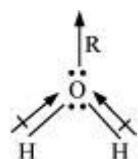
Q.7. Although both CO_2 and H_2O are triatomic molecules, the shape of H_2O molecule is bent while that of CO_2 is linear. Explain this on the basis of dipole moment.

Ans- According to experimental results, the dipole moment of carbon dioxide is zero. This is possible only if the molecule is linear so that the dipole moments of C–O bonds are equal and opposite to nullify each other.



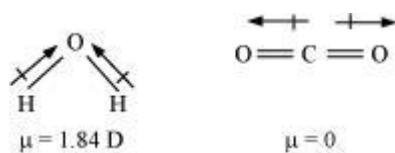
Resultant $\mu = 0 \text{ D}$

H_2O , on the other hand, has a dipole moment value of 1.84 D (though it is a triatomic molecule as CO_2). The value of the dipole moment suggests that the structure of H_2O molecule is bent where the dipole moment of O–H bonds are unequal.



Q.8. Write the significance/applications of dipole moment.

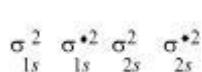
Ans- Dipole moment is the measure of the polarity of a bond. It is used to differentiate between polar and non-polar bonds since all non-polar molecules (e.g. H_2 , O_2) have zero dipole moments. It is also helpful in calculating the percentage ionic character of a molecule.



Q.9. Use molecular orbital theory to explain why the Be_2 molecule does not exist.

Ans- The electronic configuration of Beryllium is $1s^2 2s^2$.

The molecular orbital electronic configuration for Be_2 molecule can be written as:



Hence, the bond order for Be_2 is $\frac{1}{2}(N_b - N_a)$.

Where,

N_b = Number of electrons in bonding orbitals

N_a = Number of electrons in anti-bonding orbitals

$$\therefore \text{Bond order of } \text{Be}_2 = \frac{1}{2}(4-4) = 0$$

A negative or zero bond order means that the molecule is unstable.
Hence, Be_2 molecule does not exist.

Q.10. Distinguish between a sigma and a pi bond.

Ans- The following are the differences between sigma and pi-bonds:

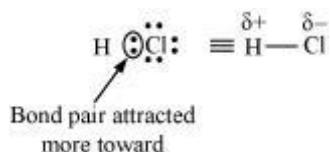
| Sigma (σ) Bond | Pi (π) Bond |
|--|---|
| (a) It is formed by the end to end overlap of orbitals. | It is formed by the lateral overlap of orbitals. |
| (b) The orbitals involved in the overlapping are $s-s$, $s-p$, or $p-p$. | These bonds are formed by the overlap of p -orbitals only. |
| (c) It is a strong bond. | It is weak bond. |
| (d) The electron cloud is symmetrical about the line joining the two nuclei. | The electron cloud is not symmetrical. |
| (e) It consists of one electron cloud, which is symmetrical about the internuclear axis. | There are two electron clouds lying above and below the plane of the atomic nuclei. |
| (f) Free rotation about σ bonds is possible. | Rotation is restricted in case of pi-bonds. |

Q.11. Explain with the help of suitable example polar covalent bond.

Ans- When two dissimilar atoms having different electronegativities combine to form a covalent bond, the bond pair of electrons is not shared equally. The bond pair shifts towards the nucleus of the atom having greater electronegativity. As a result, electron distribution gets distorted and the electron cloud is displaced towards the electronegative atom.

As a result, the electronegative atom becomes slightly negatively charged while the other atom becomes slightly positively charged. Thus, opposite poles are developed in the molecule and this type of a bond is called a polar covalent bond.

HCl, for example, contains a polar covalent bond. Chlorine atom is more electronegative than hydrogen atom. Hence, the bond pair lies towards chlorine and therefore, it acquires a partial negative charge.



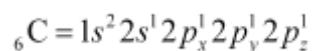
THREE MARKS QUESTIONS

Q.1. Write Lewis dot symbols for atoms of the following elements: Mg, Na, B, O, N, Br.

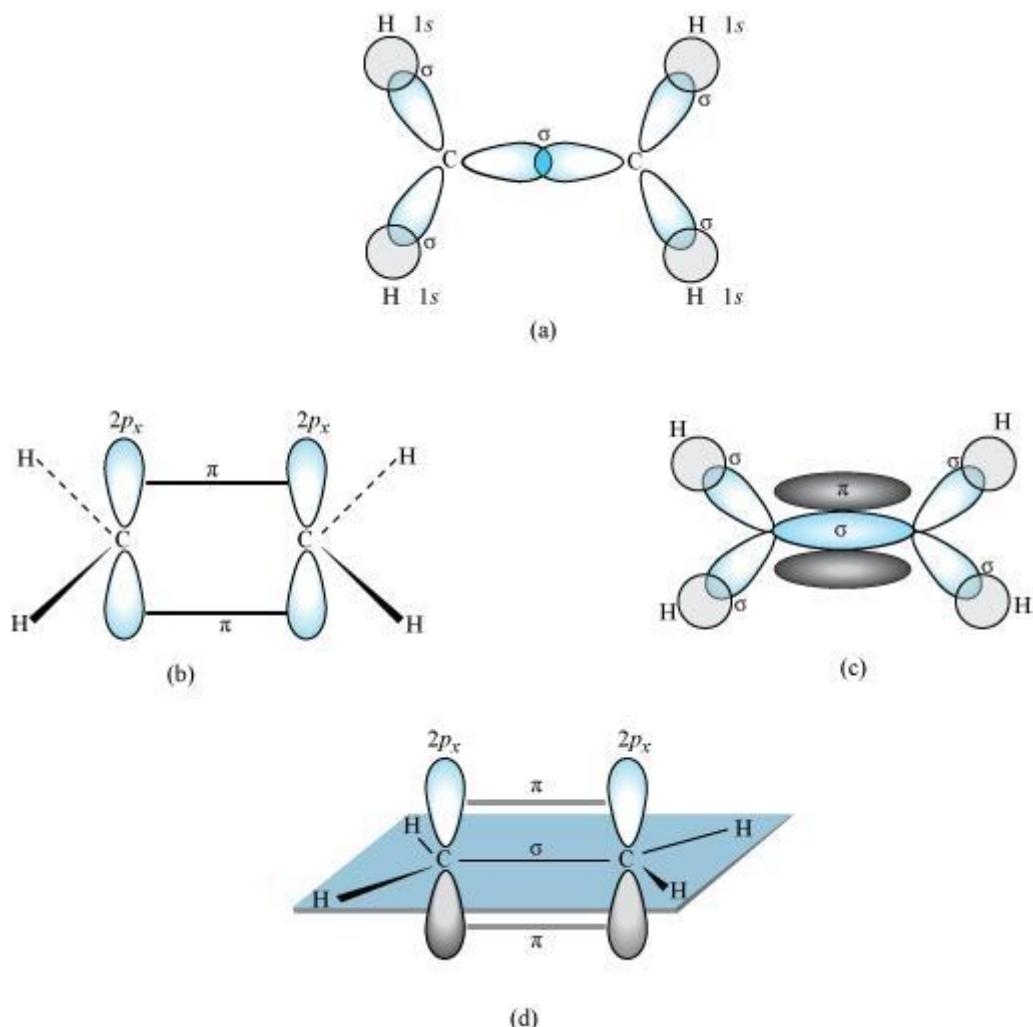
Ans- Mg: Na[.] •B• :[.]:O:[.] :[.]:N:[.] :[.]:Br:[.]

Q.3. Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in C₂H₄ and C₂H₂ molecules.

Ans- C₂H₄: The electronic configuration of C-atom in the excited state is:



In the formation of an ethane molecule (C₂H₄), one sp^2 hybrid orbital of carbon overlaps a sp^2 hybridized orbital of another carbon atom, thereby forming a C-C sigma bond. The remaining two sp^2 orbitals of each carbon atom form a sp^2-s sigma bond with two hydrogen atoms. The unhybridized orbital of one carbon atom undergoes sidewise overlap with the orbital of a similar kind present on another carbon atom to form a weak π -bond.

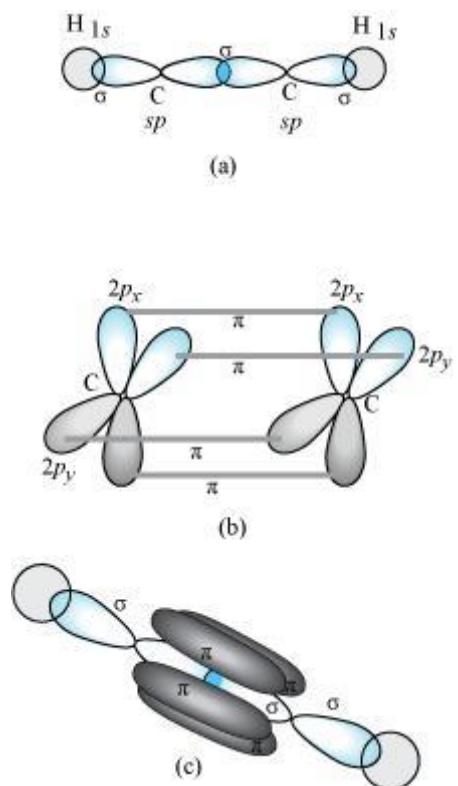


C₂H₂:

In the formation of C₂H₂ molecule, each C–atom is *sp* hybridized with two 2*p*-orbitals in an unhybridized state.

One *sp* orbital of each carbon atom overlaps with the other along the internuclear axis forming a C–C sigma bond. The second *sp* orbital of each C–atom overlaps a half-filled 1s-orbital to form a σ bond.

The two unhybridized 2*p*-orbitals of the first carbon undergo sidewise overlap with the 2*p* orbital of another carbon atom, thereby forming two pi (π) bonds between carbon atoms. Hence, the triple bond between two carbon atoms is made up of one sigma and two π -bonds.



Q.4. Explain the formation of H_2 molecule on the basis of valence bond theory.

Ans- Let us assume that two hydrogen atoms (A and B) with nuclei (N_A and N_B) and electrons (e_A and e_B) are taken to undergo a reaction to form a hydrogen molecule. When A and B are at a large distance, there is no interaction between them. As they begin to approach each other, the attractive and repulsive forces start operating.

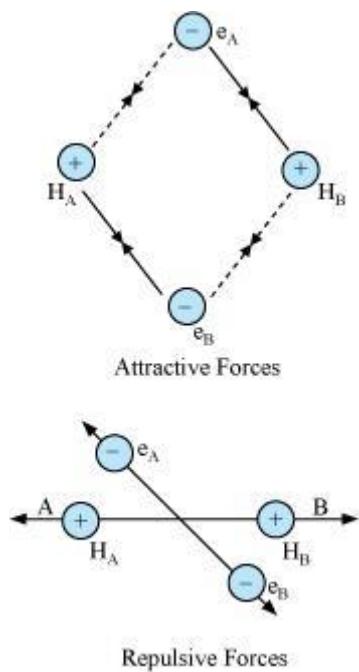
Attractive force arises between:

- (a) Nucleus of one atom and its own electron i.e., $N_A - e_A$ and $N_B - e_B$.
- (b) Nucleus of one atom and electron of another atom i.e., $N_A - e_B$ and $N_B - e_A$.

Repulsive force arises between:

- (a) Electrons of two atoms i.e., $e_A - e_B$.
- (b) Nuclei of two atoms i.e., $N_A - N_B$.

The force of attraction brings the two atoms together, whereas the force of repulsion tends to push them apart.



The magnitude of the attractive forces is more than that of the repulsive forces. Hence, the two atoms approach each other. As a result, the potential energy decreases. Finally, a state is reached when the attractive forces balance the repulsive forces and the system acquires minimum energy. This leads to the formation of a dihydrogen molecule.

Q.5. Write the important conditions required for the linear combination of atomic orbitals to form molecular orbitals.

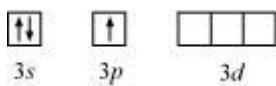
Ans- The given conditions should be satisfied by atomic orbitals to form molecular orbitals:

- (a) The combining atomic orbitals must have the same or nearly the same energy. This means that in a homonuclear molecule, the $1s$ -atomic orbital of an atom can combine with the $1s$ -atomic orbital of another atom, and not with the $2s$ -orbital.
- (b) The combining atomic orbitals must have proper orientations to ensure that the overlap is maximum.
- (c) The extent of overlapping should be large.

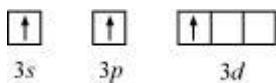
Q.6. Describe the hybridisation in case of PCl_5 . Why are the axial bonds longer as compared to equatorial bonds?

Ans- The ground state and excited state outer electronic configurations of phosphorus ($Z = 15$) are:

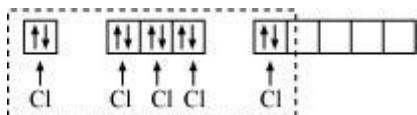
Ground state:



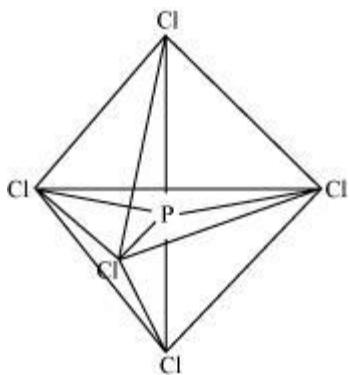
Excited state:



Phosphorus atom is sp^3d hybridized in the excited state. These orbitals are filled by the electron pairs donated by five Cl atoms as:



The five sp^3d hybrid orbitals are directed towards the five corners of the trigonal bipyramidal. Hence, the geometry of PCl_5 can be represented as:



There are five P–Cl sigma bonds in PCl_5 . Three P–Cl bonds lie in one plane and make an angle of 120° with each other. These bonds are called equatorial bonds. The remaining two P–Cl bonds lie above and below the equatorial plane and make an angle of 90° with the plane. These bonds are called axial bonds.

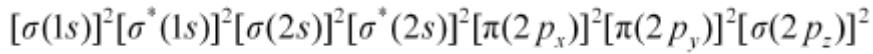
As the axial bond pairs suffer more repulsion from the equatorial bond pairs, axial bonds are slightly longer than equatorial bonds.

Q.7. What is meant by the term bond order? Calculate the bond order of: N_2 , O_2 , O_2^+ and O_2^- .

Ans- Bond order is defined as one half of the difference between the number of electrons present in the bonding and anti-bonding orbitals of a molecule.

$$\text{Bond order} = \frac{1}{2}(N_b - N_a)$$

Bond order of N_2

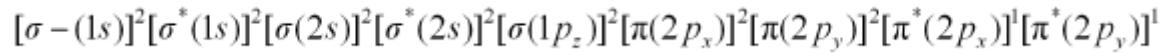


Number of bonding electrons, $N_b = 10$

Number of anti-bonding electrons, $N_a = 4$

$$\text{Bond order of nitrogen molecule} = \frac{1}{2}(10 - 4) = 3$$

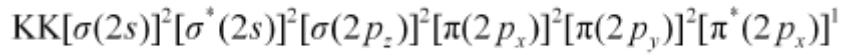
Bond order of O_2



$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(8 - 4) = 2$$

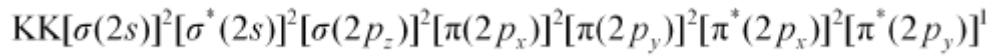
Hence, the bond order of oxygen molecule is 2.

Similarly, the electronic configuration of O_2^+ can be written as:



$$\text{Bond order of } \text{O}_2^+ = \frac{1}{2}(8 - 3) = 2.5$$

The electronic configuration of O_2^- ion will be:



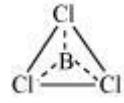
$$\text{Bond order of } \text{O}_2^- = \frac{1}{2}(8 - 5) = 1.5$$

Q.8. Discuss the shape of the following molecules using the VSEPR model:

BeCl_2 , BCl_3 , SiCl_4 , AsF_5 , H_2S , PH_3

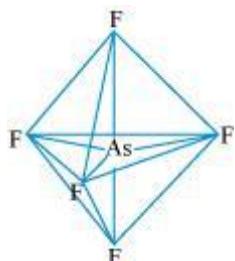
Ans- BeCl_2 : $\text{Cl}:\text{Be}:\text{Cl}$ The central atom has no lone pair and there are two bond pairs. i.e., BeCl_2 is of the type AB_2 . Hence, it has a linear shape.

BCl_3 : $\begin{array}{c} \text{Cl} \\ | \\ \text{Cl}-\text{B}-\text{Cl} \\ | \\ \text{Cl} \end{array}$ The central atom has no lone pair and there are three bond pairs.



Hence, it is of the type AB_3 . Hence, it is trigonal planar.

SiCl_4 : $\begin{array}{c} \text{Cl} \\ | \\ \text{Cl}-\text{Si}-\text{Cl} \\ | \\ \text{Cl} \end{array}$ The central atom has no lone pair and there are four bond pairs. Hence, the shape of SiCl_4 is tetrahedral being the AB_4 type molecule.



AsF_5 : The central atom has no lone pair and there are five bond pairs. Hence, AsF_5 is of the type AB_5 . Therefore, the shape is trigonal bipyramidal.

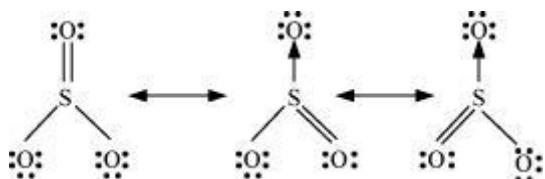
H_2S : $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{S}-\text{H} \\ | \\ \text{H} \end{array}$ The central atom has one lone pair and there are two bond pairs. Hence, H_2S is of the type AB_2E . The shape is Bent.

PH_3 : $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{P}-\text{H} \\ | \\ \text{H} \end{array}$ The central atom has one lone pair and there are three bond pairs. Hence, PH_3 is of the AB_3E type. Therefore, the shape is trigonal bipyramidal.

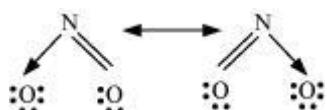
Q.9. Write the resonance structures for SO_3 , NO_2 and NO_3^- .

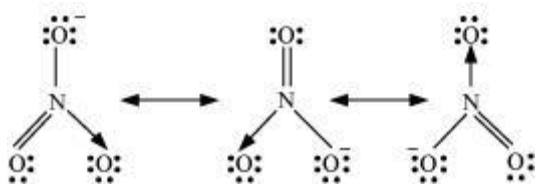
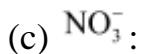
Ans- The resonance structures are:

(a) SO_3 :



(b) NO_2 :

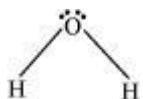




Q.10. What do you understand by bond pairs and lone pairs of electrons? Illustrate by giving example.

Ans- The shared pairs of electrons present between the bonded atoms are called **bond pairs**. All valence electrons may not participate in bonding. The electron pairs that do not participate in bonding are called **lone pairs** of electrons.

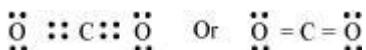
In H_2O , there are two bond pairs and two lone pairs on the central atom (oxygen).



FIVE MARKS QUESTIONS

Q.1. Define octet rule. Write its significance and limitations.

Ans-- The octet rule or the electronic theory of chemical bonding was developed by Kossel and Lewis. According to this rule, atoms can combine either by transfer of valence electrons from one atom to another or by sharing their valence electrons in order to attain the nearest noble gas configuration by having an octet in their valence shell.



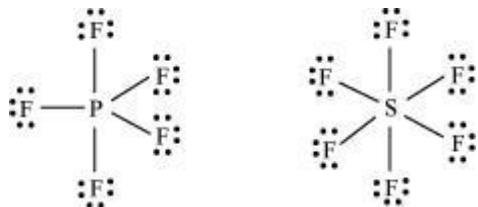
The octet rule successfully explained the formation of chemical bonds depending upon the nature of the element.

Limitations of the octet theory:

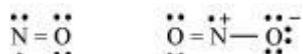
The following are the limitations of the octet rule:

- The rule failed to predict the shape and relative stability of molecules.
- It is based upon the inert nature of noble gases. However, some noble gases like xenon and krypton form compounds such as XeF_2 , KrF_2 etc.

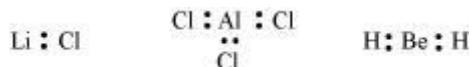
(c) The octet rule cannot be applied to the elements in and beyond the third period of the periodic table. The elements present in these periods have more than eight valence electrons around the central atom. For example: PF_5 , SF_6 , etc.



(d) The octet rule is not satisfied for all atoms in a molecule having an odd number of electrons. For example, NO and NO_2 do not satisfy the octet rule.



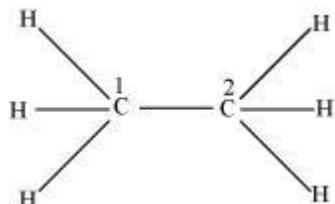
(e) This rule cannot be applied to those compounds in which the number of electrons surrounding the central atom is less than eight. For example, LiCl , BeH_2 , AlCl_3 etc. do not obey the octet rule.



Q.2. Which hybrid orbitals are used by carbon atoms in the following molecules?

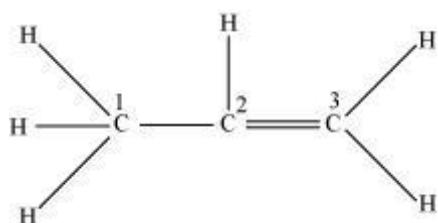
(a) CH_3-CH_3 ; (b) $\text{CH}_3-\text{CH}=\text{CH}_2$; (c) $\text{CH}_3-\text{CH}_2-\text{OH}$; (d) CH_3-CHO (e) CH_3COOH

Ans- (a)



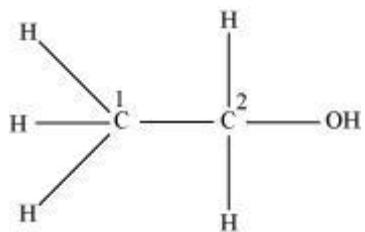
Both C₁ and C₂ are sp^3 hybridized.

(b)



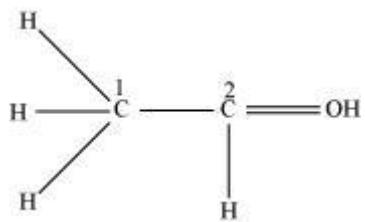
C_1 is sp^3 hybridized, while C_2 and C_3 are sp^2 hybridized.

(c)



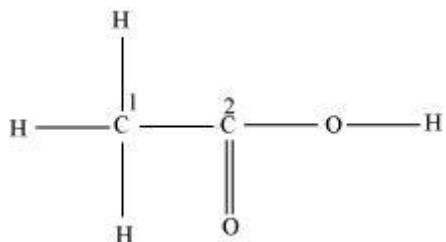
Both C_1 and C_2 are sp^3 hybridized.

(d)



C_1 is sp^3 hybridized and C_2 is sp^2 hybridized.

(e)



C_1 is sp^3 hybridized and C_2 is sp^2 hybridized.

Q.3. Compare the relative stability of the following species and indicate their magnetic properties;

O_2 , O_2^+ , O_2^- (superoxide), O_2^{2-} (peroxide)

Ans- There are 16 electrons in a molecule of dioxygen, 8 from each oxygen atom. The electronic configuration of oxygen molecule can be written as:

$[\sigma - (1s)]^2 [\sigma^* (1s)]^2 [\sigma (2s)]^2 [\sigma^* (2s)]^2 [\sigma (1p_z)]^2 [\pi (2p_x)]^2 [\pi^* (2p_x)]^1 [\pi (2p_y)]^2 [\pi^* (2p_y)]^1$

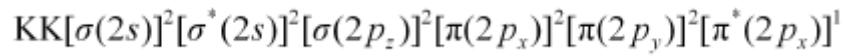
Since the $1s$ orbital of each oxygen atom is not involved in bonding, the number of bonding electrons = 8 = N_b and the number of anti-bonding orbitals = 4 = N_a .

$$\text{Bond order} = \frac{1}{2}(N_b - N_a)$$

$$= \frac{1}{2}(8 - 4)$$

$$= 2$$

Similarly, the electronic configuration of O_2^+ can be written as:



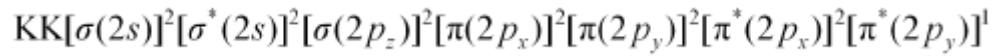
$$N_b = 8$$

$$N_a = 3$$

$$\text{Bond order of } \text{O}_2^+ = \frac{1}{2}(8 - 3)$$

$$= 2.5$$

Electronic configuration of O_2^- ion will be:



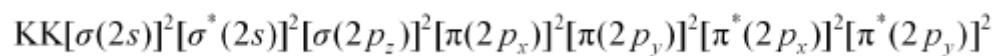
$$N_b = 8$$

$$N_a = 5$$

$$\text{Bond order of } \text{O}_2^- = \frac{1}{2}(8 - 5)$$

$$= 1.5$$

Electronic configuration of O_2^{2-} ion will be:



$$N_b = 8$$

$$N_a = 6$$

Bond order of $O_2^{2-} = \frac{1}{2}(8 - 6)$

$$= 1$$

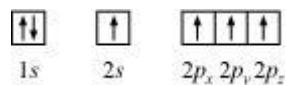
Bond dissociation energy is directly proportional to bond order. Thus, the higher the bond order, the greater will be the stability. On this basis, the order of stability is $O_2^+ > O_2 > O_2^- > O_2^{2-}$.

HOTS

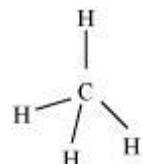
Q.1. Apart from tetrahedral geometry, another possible geometry for CH_4 is square planar with the four H atoms at the corners of the square and the C atom at its centre. Explain why CH_4 is not square planar?

Ans- Electronic configuration of carbon atom: $_6C: 1s^2 2s^2 2p^2$

In the excited state, the orbital picture of carbon can be represented as:



Hence, carbon atom undergoes sp^3 hybridization in CH_4 molecule and takes a tetrahedral shape.



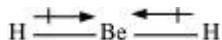
For a square planar shape, the hybridization of the central atom has to be dsp^2 . However, an atom of carbon does not have d -orbitalsto undergo dsp^2 hybridization. Hence, the structure of CH_4 cannot be square planar.

Moreover, with a bond angle of 90° in square planar, the stability of CH_4 will be very less because of the repulsion existing between the bond pairs. Hence, VSEPR theory also supports a tetrahedral structure for CH_4 .

Q.2. Explain why BeH_2 molecule has a zero dipole moment although the Be–H bonds are polar.

Ans- The Lewis structure for BeH_2 is as follows: $\text{H}:\text{Be}:\text{H}$

There is no lone pair at the central atom (Be) and there are two bond pairs. Hence, BeH_2 is of the type AB_2 . It has a linear structure.

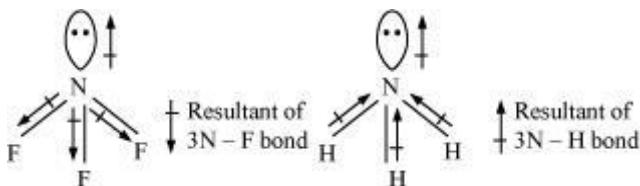


Dipole moments of each H–Be bond are equal and are in opposite directions. Therefore, they nullify each other. Hence, BeH_2 molecule has zero dipole moment.

Q.3. Which out of NH_3 and NF_3 has higher dipole moment and why?

Ans- In both molecules i.e., NH_3 and NF_3 , the central atom (N) has a lone pair electron and there are three bond pairs. Hence, both molecules have a pyramidal shape. Since fluorine is more electronegative than hydrogen, it is expected that the net dipole moment of NF_3 is greater than NH_3 . However, the net dipole moment of NH_3 (1.46 D) is greater than that of NF_3 (0.24 D).

This can be explained on the basis of the directions of the dipole moments of each individual bond in NF_3 and NH_3 . These directions can be shown as:



Thus, the resultant moment of the N–H bonds add up to the bond moment of the lone pair (the two being in the same direction), whereas that of the three N – F bonds partly cancels the moment of the lone pair.

Hence, the net dipole moment of NF_3 is less than that of NH_3 .

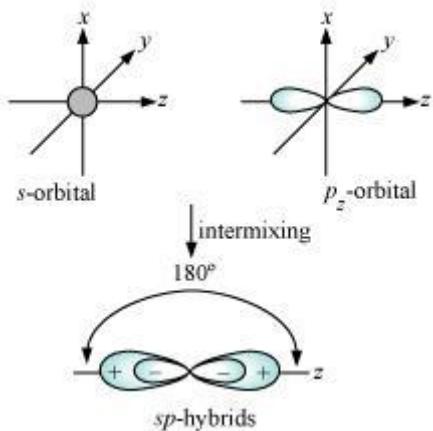
Q.4. What is meant by hybridisation of atomic orbitals? Describe the shapes of sp , sp^2 , sp^3 hybrid orbitals.

Ans- Hybridization is defined as an intermixing of a set of atomic orbitals of slightly different energies, thereby forming a new set of orbitals having equivalent energies and shapes.

For example, one $2s$ -orbital hybridizes with two $2p$ -orbitals of carbon to form three new sp^2 hybrid orbitals.

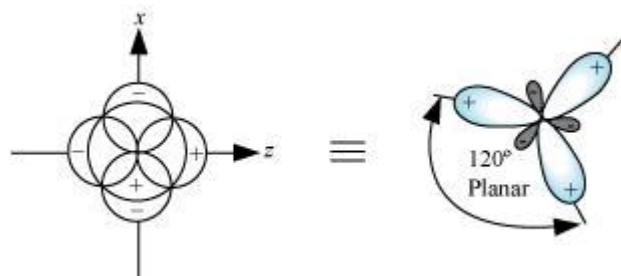
These hybrid orbitals have minimum repulsion between their electron pairs and thus, are more stable. Hybridization helps indicate the geometry of the molecule.

Shape of sp hybrid orbitals: sp hybrid orbitals have a linear shape. They are formed by the intermixing of s and p orbitals as:



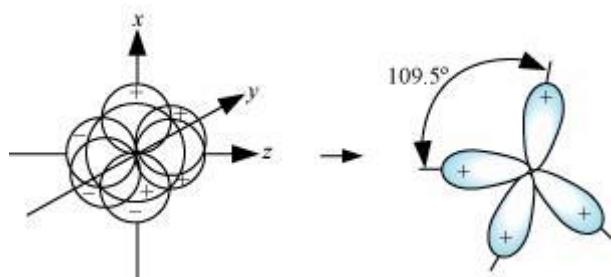
Shape of sp^2 hybrid orbitals:

sp^2 hybrid orbitals are formed as a result of the intermixing of one s -orbital and two p -orbitals. The hybrid orbitals are oriented in a trigonal planar arrangement as:



Shape of sp^3 hybrid orbitals:

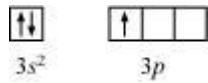
Four sp^3 hybrid orbitals are formed by intermixing one s -orbital with three p -orbitals. The four sp^3 hybrid orbitals are arranged in the form of a tetrahedron as:



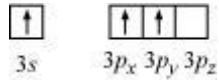
Q.5. Describe the change in hybridisation (if any) of the Al atom in the following reaction.



Ans- The valence orbital picture of aluminium in the ground state can be represented as:



The orbital picture of aluminium in the excited state can be represented as:



Hence, it undergoes sp^2 hybridization to give a trigonal planar arrangement (in AlCl_3).

To form AlCl_4^- , the empty $3p_z$ orbital also gets involved and the hybridization changes from sp^2 to sp^3 . As a result, the shape gets changed to tetrahedral.

CHAPTER 5

STATES OF MATTER

1. **Change in state** : It is over all effect of Intermolecular forces, molecular Interactional energy & thermal energy:
2. **Measurable properties of gases** : P,V, T, n, Viscosity, specific heat are some measurable properties.
3. **Gas Laws** : The quantitative relationship b/w any two of the variables (V, n, P,T) when other two are constant.
4. Boyle's Law : The pressure of fixed msss of gas varies inversely with the volume at constant T. $P \propto 1/V(n,T \text{ const.})$

$$P_1 V_1 = P_2 V_2$$

5. **Charle's Law** : At constant P, the volume of fixed amount of gas varies directly with its absolute temperature.

$$V \propto T \quad \text{or} \quad \frac{V}{T} = \text{constant}, \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

6. **Gay lussac's Law** : At constant V, The pressure of fixed amount of gas varies directly with its absolute temperature.

$$P \propto T \quad \text{or} \quad \frac{P}{T} = \text{const}, \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

7. Ideal gas equation : The relationship b/w P, V and T by Gas Laws $PV = nRT$.
8. Avogadro's Law : At given T and P, the volume of gas varies directly to the amount of gas . $V \propto n (P, T \text{ constant})$
9. Dalton's Law of partial persure : The pressure enerted by a mixture of non reacting gases is equal to the sum of their partial pressure at constant (V,T)

$$P(\text{total}) = P_1 + P_2 + P_3 + \dots \quad (\text{T, V, constant})$$

10. Kinetic Molecular theory :

- a. Gases consist of large number of identical particles (atoms or molecules) that are so small that the actual volume of the molecules is negligible in comparison to the empty space between them.
- b. There is no force of attraction between the particles of a gas at ordinary temperature and pressure
- c. Particles of a gas are always in constant and random motion
- d. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container
- e. Collisions of gas molecules are perfectly elastic
- f. At any particular time, different particles in the gas have different speeds and hence different kinetic energies
- g. Average kinetic energy of the gas molecules is directly proportional to the absolute temperature

11. Real Gases : The gases which deviates from Ideal behavior at higher pressure and low temperature b/c of force of attraction b/w molecules increases .

12. Compressibility factor (Z) : It determine extent of deviation

$$\text{of real gases from Ideal gas behavior : } Z = \frac{PV}{n.R.T.} \quad \text{for ideal}$$

gas $Z=1$, for Nonideal gas $Z < 1$, $Z > 1$

13. Vander waal's Equation : $\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$.

14. Critical Temperature : (T_c) The temperature above which a gas cannot be liquefied whatever high pressure may be

15. Critical Pressure : The minimum pressure required to liquify a gas at its critical temperature.

16. Critical Volume : The volume of 1 mole of gas at T_c , P_c .

17. Super cooled liquids : The liquids which are cooled to a temperature below its freezing point without freezing .

18. Elastic Collision : The collisions in which no loss of K.E. only there is transfer of energy.
19. Vapour pressure : The equilibrium pressure by vapour of liquid in a container at given temperature (T)
20. At higher altitude : The b.p. of water decreases b/c the atmospheric pressure is less than one atmosphere.
21. Surface Tension (V) : It is force acting per unit length perpendicular to the line drawn on the surface : (Nm^{-1}) : It decreases with increases in T, it increases with increase in external pressure, b/c of it falling drops of liquid are spherical, liquid in capillary tube rises.
22. Viscosity (η) : It is resistance offered to the flow of liquid due to friction b/w layer of fluids . $F = n.A.\frac{dv}{dn}$
23. Effect of T & P on viscosity : It decreases with increase in T, and increases with increase in P.
24. Low M.P. & B.P. of molecular liquids is due to low magnitude of molecular interaction energy.

One mark questions

1. At what condition surface tension vanishes ?
2. Why Helium is used in balloons in place of hydrogen?
3. At what temperature below which a gas does not obey ideal gas law?
4. At what temperature the volume of a gas is supposed to be zero?
5. What is the molar volume at 0°C and 1 bar pressure?

6. Name the temperature above which a gas cannot be liquefied by any amount of pressure.
7. What is the effect of increase of temperature on surface tension and viscosity in a liquid?
8. How is the partial pressure of a gas in a mixture related to the total pressure of the gaseous mixture?
9. Why vegetables are cooked with difficulty at hill station.
10. What is the value of Z (compressibility factor) for an Ideal gas?

Answers to One mark questions

- Ans 1 At critical temperature, meniscus b/w liquid and vapours disappears.
- Ans 2. He is incombustible , though heavier than H₂.
- Ans 3. Below Boyle Temperature.
- Ans 4. At absolute zero (O K) temperature.
- Ans 5. It 22400 ml.
- Ans 6. It is critical temperature (Tc)
- Ans 7. Both decreases with increase in temperature
- Ans 8. $P_1 = X_1 \times P_{\text{total}}$
- Ans 9. At hill station the atmospheric pressure is less and so boiling point decreases.
- Ans10. For ideal gas Z=1.

Two Marks Questions

- Q.1 How do you convert pressure in atmosphere in to SI unit.

- Q.2 What type graph will you get when PV is plotted against P at constant temperature.
- Q.3 What would have happened to the gas if the molecular collisions were not elastic?
- Q.4 At a particular temperature, why vapour pressure of acetone is less than of ether?
- Q.5 Why liquids diffuse slowly as compared to gases?
- Q.6 What would be the SI unit for quantity $\frac{P \cdot V^2 \cdot T^2}{n}$?
- Q.7 In terms of Charle's law explain why -273°C is the lowest temperature?
- Q.8 For real gases the relation b/w P,V,T is given by vander Waal's equation, write it for n moles?
- Q.9 What correction is applied to obtain pressure of dry gas with the total pressure & aqueous tension?
- Q.10 Name two phenomena that can be explained on the basis of surface tension.

Answers to two marks questions

Ans 1. $1\text{atm} = 101325 \text{ Pa}$ or Nm^{-2} , $1 \text{ bar} = 10^5 \text{ Pa}$.

Ans 2 .A straight line parallel to pressure axis.

Ans 3. On every collision there is loss of energy, so molecules would have slowed down & settled down in vessel and pressure reduce to O.

Ans 4. b/c molecular force of attraction in acetone is stronger than those present in ether.

Ans 5. In liquids the molecules are less free than in a gas. i. e intermolecular forces in liquid are greater than in gas.

Ans 6.
$$\frac{P \cdot V^2 \cdot T^2}{n} = \frac{(V \cdot m^{-2})^2 (K)^2}{mol} = N \cdot m^4 \cdot k^2 \cdot mol^{-1}$$

Ans 7 At $-273^\circ C$, the Volume of gas becomes equal to zero i. e. gas ceases to exist.

Ans 8. Vander waal's equation

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = n \cdot R \cdot T.$$

Ans 9. $P_{(\text{dry gas})} = P_{(\text{Total})} - \text{Aqueous tension}$

Ans 10. Surface tension can explain (i) capillary action. (ii) Spherical shape of small drops of liquid.

Three Marks Questions

Q.1 Calculate temperature of 4.0 moles of gas occupying $5dm^3$ volume at 3.32 bar. ($R = 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$)

Ans $PV = nRT, \text{ or } T = \frac{PV}{nR}$

Or $T = \frac{3.32 \text{ bar} \times 5dm^3}{4.0\text{mol} \times 0.083bar \text{ dm}^3 \text{ K}^{-1} \text{ mol}^{-1}} = 50. Ans$

Q.2 34.05 ml of phosphorus vapours weight 0.0625g at $543^\circ C$ and 1 bar pressure what is molar mass of phosphorous?

Ans. $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}, \Rightarrow \frac{1 \times 34.05}{(54b+273)} = \frac{1 \times v_2}{273} \text{ at } 0^\circ C$

Or $V_2 = 11.35 \text{ ml}$

Now 11.35 ml of vapours at $0^\circ C$ and 1 bar pressure weight 0.0625 gm

Now 22700 ml of vapors at 0° C and 1 bar pressure weight

$$\frac{0.0625}{11.35} \times 22700$$

- Q.3 A mixture of dihydrogen and dinitrogen at 1 bar pressure contains 20% by weight of H₂. Calculate partial pressure of H₂.

Ans The mixture of H₂ and O₂ contain 20% H₂ means 20 gm H₂ & 80gm O₂

$$n_2(H_2) = \frac{20}{2} = 10 \text{ moles}, n(O_2) = \frac{80}{32} = 2.5 \text{ contest.}$$

$$P_{(H_2)} = \frac{n(H_2)}{n(H_2) + n(V_2)} \times P_{(total)} = \frac{10}{10 + 2.5} \times 1 \text{ bar} = 0.8 \text{ bar}$$

- Q.4 What will be minimum pressure required compressing 500dm³ of air at 1 bar to 200 dm³ at 30° C?

Ans. P₁ = 1bar. V₁ = 500dm³

$$P_2 = ? \quad V_2 = 200 \text{ dm}^3 \quad \& \text{ temp. constant } 30^\circ \text{C}$$

So by Boyle's law P₁V₁ = P₂V₂

$$1 \times 500 = P_2 \times 200 \quad \text{or } P_2 \frac{500}{200} = 2.5 \text{ bar}$$

- Q.5 Calculate the total pressure in mixture of 4g of O₂ and 2gm. Of H₂ can fixed to a total volume of 1L at 0° C. (R = 0.0821) Latm. Mol⁻¹

$$\text{Ans } P = \cancel{4o_2 + nH_2} \times \frac{RT}{V}$$

$$= \left(\frac{4}{32} + \frac{2}{2} \right) \times \frac{0.0821 \times 273}{1} = \left(\frac{1}{8} + 1 \right) 22.4 = 25.2 \text{ atm. Ans}$$

- Q.6 Account for the following :

- (i) The size of weather balloon becomes longer and larger as it ascends up into higher altitudes.

Ans (i) At higher altitudes atmospheric pressure decreases, but inside the balloon gas exerts pressure and size becomes larger.

Q.8 What do you mean by ideal gas and real gas? Why do real gases deviate from ideal behaviors?

Ans. Ideal gas follows gas laws at all P & T

Real gas does not follow gas laws at all P & T.

Real gas deviates from ideal behaviour due to force of attraction and because of volume of molecules of gases are not negligible.

Q.9 Using the equation of state $PV=nRT$ Show that at given T, density of gas proportional to gas pressure P.

$$PV = nRT \Rightarrow P = \frac{n}{v} \cdot RT$$

$$\Rightarrow P = \frac{m}{M} \cdot \frac{1}{V} \cdot RT, R.T. = \frac{m}{V} \cdot \frac{RT}{M}$$

$$\Rightarrow P = P \cdot \frac{RT}{M} \quad (\text{Where } P = \frac{m}{v})$$

$$\Rightarrow P \propto P \left(\because \frac{RT}{M} = \text{const.} \right)$$

Q.10 Critical temperature of CO_2 and CH_4 gases are 31.1°C and -81.9°C respectively. Which of these has strong intermolecular forces & why?

Ans CO_2 has strong van der waal's forces of attraction than CH_4 b/c of greater polarity and high molecular wt.

Hots Questions with Answers.

- Q.1 (a) Why aerated water bottles kept under water during summer?
(b) Which property of liquid is responsible for spherical shape of drop?
(c) Why is moist air lighter than dry air?
(d) Define aqueous tension?
(e) What are units of a and b which are vander waal's constant?

- Ans (a) To reduce temperature so to reduce pressure, otherwise bottle may burst.
(b) Surface Tension.
(c) Moist air has water vapours which lowers vapour density, so it is lighter.
(d) It is pressure of water vapours at given T.
(e) Unit of a in atm. $L^2 \text{ mol}^{-2}$, b is $L \text{ mol}^{-1}$.

- Q.2 Why does sharpened edge becomes smooth on heating up to melting point?

Ans On heating the glass it melts and take up rounded shape at edges which has minimum surface area. b/c of surface tension.

- Q.3 Arrange following in order of increasing density:

$$d = \frac{PM}{RT}, O_2 \text{ at } 25^\circ C, 1\text{atm}, O_2 \text{ at } 0^\circ C, 2\text{atm}, O_2 \text{ at } 273^\circ C, 1\text{atm}.$$

Ans $d = \frac{PM}{RT}$, R, M are constant, so d depends upon $\frac{P}{T}$ so at $25^\circ C$,

$1\text{Atm} \frac{P}{T} = \frac{1}{298}$, At $273^\circ C$, $1\text{atm} \frac{P}{T} = \frac{1}{546}$ Hence increasing order of density will be: O_2 at $273^\circ C, 1\text{atm} < O_2$ at $25^\circ C, 2\text{atm}$.

- Q.4 An O_2 cylinder has 10L O_2 at 200 atm. If patient takes 0.50ml of O_2 at 1 atm in one breath at $37^\circ C$. How many breaths are possible?

Ans $10\text{L at } 200 \text{ atm} = ? \text{ L at } 1\text{atm} \Rightarrow P, V = P_2 V_2 \Rightarrow 200 \times 10 = 1 \times V_2$ or

$$V_2 = 2000 \text{ L, No of breathes} = \frac{\text{Total Volume}}{\text{Volume for 1 breath}} = \frac{2000 \text{ L}}{0.5 \times 10^{-3} \text{ L}} = 4 \times 10^6$$

CHAPTER 6 **THERMODYNAMICS”**

Brief Summary of the chapter:

1. Thermodynamics: Science which deals with study of different forms of energy and quantitative relationship.
2. System & Surroundings: The part of universe for study is called system and remaining portion is surroundings.
3. State of system & state function: State of system is described in terms of T, P, V etc. The property which depends only on state of system not upon path is called state function eg. P, V, T, E, H, S etc.
4. Extensive & Intensive Properties: Properties which depends on quantity of matter called extensive prop. eg. mass, volume, heat capacity, enthalpy, entropy etc. The properties which do not depends on matter present depends upon nature of substance called Intensive properties. eg. T,P, density, refractive index, viscosity, bp, pH, mole fraction etc.
5. Internal energy: The total energy with a system.

$$\text{i.e. } U = E_e + E_n + E_c + E_p + E_k + \dots$$

$\Delta U = U_2 - U_1$ or $U_p - U_R$ & U is state function and extensive property. If $U_1 > U_2$ energy is released.

6. Heat (q): It is a form of energy which is exchanged between system and surrounding due to difference of temperature. Unit is Joule (J) or Calorie (1 Calorie = $4.18 \mu J$).
7. First Law of Thermodynamics: It is law of conservation of energy. Energy can neither be created nor destroyed, it may be converted from one form into another.

Mathematically $\Delta U = q + w$, $w = -p \cdot \Delta V$ (work of expansion)

$\Delta U = q - p \cdot \Delta V$ or $q = \Delta U + p \cdot \Delta V$, q,w are not state function.

But ΔU is state function.

8. Enthalpy (H): At constant volume $\Delta V = 0$, $\rightarrow q_v = \Delta U$

$$\text{So } H = U + p \cdot \Delta V, q_p = H_2 - H_1 = \Delta H$$

$$\Rightarrow \Delta H = \Delta U + P \cdot \Delta V.$$

9. Relationship between q_p , q_v i.e. $\Delta H & \Delta U$

$$\text{It is } \Delta H = \Delta U + \Delta n g \cdot RT \text{ or } q_p = q_v + \Delta n g \cdot RT$$

10. Exothermic and Endothermic reactions: $\Delta H = -Ve$ for exothermic and $\Delta H = +Ve$ for endothermic reaction i.e. evolution and absorption of heat.



11. Enthalpy of reaction ($\Delta_r H$): The amount of heat evolved or absorbed when the reaction is completed.

12. Standard Enthalpy of reaction ($\Delta_r H^0$) at 1 bar pressure and specific temp. (290K) i.e. standard state.

13. Different types of Enthalpies of reactions:

(i) Enthalpy of combustion ($\Delta_c H$), (ii) Enthalpy of formation ($\Delta_f H$)

(iii) Enthalpy of neutralization (iv) Enthalpy of solution

(v) Enthalpy of atomization($\Delta_a H$), (vi) Enthalpy of Ionisation ($\Delta_i H$)

(vii) Enthalpy of Hydration ($\Delta_{hyol.} H$) (viii) Enthalpy of fusion ($\Delta_{fus.} H$)

(ix) Enthalpy of vaporization ($\Delta_{vap.} H$) (x) Enthalpy of sublimation ($\Delta_{sub.} H$)

$$(\Delta_{sub.} H) = \Delta_{fus.}(H) - \Delta_{vap.}(H)$$

14. Hess's Law of constant heat summation: The total amount of heat change is same whether the reaction takes place in one step or in several steps.

$$\text{i.e. } \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \dots$$

15. Bond enthalpy: It is amount of energy released when gaseous atoms combines to form one mole of bonds between them or heat absorbed when one mole of bonds between them are broken to give free gaseous atoms. Further $\Delta_r H = \sum B.E. (\text{Reactants}) - \sum B.E. (\text{Products})$
16. Spontaneous & Non Spontaneous Processes: A process which can take place by itself is called spontaneous process. A process which can neither take place by itself or by initiation is called non Spontaneous.
17. Driving forces for spontaneous process: (i) Tendency for minimum energy state. (ii) Tendency for maximum randomness.
18. Entropy (S): It is measure of randomness or disorder of system.
i.e. Gas > Liquid > Solid.

$$\text{Entropy change } (\Delta S) = \frac{q_{(\text{rev.})}}{T} \text{ J.K}^{-1} \cdot \text{mol}^{-1}$$

19. Spontaneity in term of (ΔS)

$$\Delta S_{(\text{total})} = \Delta S_{(\text{universe})} = \Delta S_{(\text{system})} + \Delta S_{(\text{surrounding})}$$

If $\Delta S_{(\text{total})}$ is +ve, the process is spontaneous.

If $\Delta S_{(\text{total})}$ is -ve, the process is non spontaneous.

20. Second Law of thermodynamics: In any spontaneous process, the entropy of the universe always increases. A spontaneous process cannot be reversed.
21. Gibb's free energy (G): defined as $G = H - T.S$ & $\Delta G = \Delta H - T. \Delta S$ (Gibb's Helmholtz equation) it is equal useful work i.e. $- \Delta G = W_{(\text{useful})} = W_{(\text{max.})}$
If $\Delta G = \text{ve}$, process is spontaneous.
22. Effects of T on spontaneity of a process: $\Delta G = \Delta H - T. \Delta S$.
 - (i) For endothermic process may be non spontaneous at low temp.

(ii) For exothermic process may be non spontaneous at high temp. and spontaneous at low temp.

23. Calculation of ($\Delta_r G^0$)

$$\Delta_r G^0 = \Sigma \Delta_f G^0 (p) - \Sigma \Delta_f G^0 (r)$$

24. Relationship between ($\Delta_r G^0$) & equilibrium constant (k)

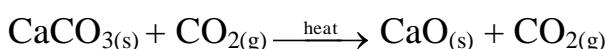
$$\Delta G = \Delta G^0 + RT \ln Q \quad \& \quad \Delta G^0 = -2.303RT \log k.$$

25. Calculation of entropy change:

$$\Delta_r S^0 = \Sigma \Delta S^0 (p) - \Sigma S^0 (r)$$

ONE MARK QUESTIONS:

1. State First Law of thermodynamics.
2. What is a thermodynamic state function?
3. Give enthalpy (H) of all elements in their standard state.
4. From thermodynamic point to which system the animals and plants belong?
5. Predict the sign of ΔS for the following reactions.



6. For the reaction $2Cl_{(g)} \rightarrow Cl_{2(g)}$, What will be the sign of ΔH and ΔS ?
7. State Hess's Law for constant heat summation?
8. What is Gibb's Helmholtz equation?
9. Define extensive properties.
10. Give relationship between ΔH , ΔU for a reaction in gaseous state.

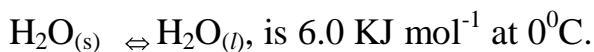
ANSWERS FOR ONE MARK QUESTIONS

1. Energy can neither be created nor destroyed. The energy of an isolated system is constant. $\Delta U = q + w$.
2. A function whose value is independent of path. eg. P, V, E, H
3. In standard state enthalpies of all elements is zero.
4. Open system.
5. ΔS is positive (entropy increases)
6. ΔH : (-ve) b/c energy is released in bond formation and
 ΔS : (-ve) b/c atoms combines to form molecules.
7. The change of enthalpy of reaction remains same, whether the reaction is carried out in one step or several steps.
8. $\Delta G = \Delta H - T \cdot \Delta S$
9. Properties which depends upon amount of substance called extensive properties. Volume, enthalpy, entropy.
10. $\Delta H = \Delta U + n g \cdot RT$.

TWO MARKS QUESTIONS:-

- Q.1 In a process, 701J heat is absorbed and 394J work is done by system. What is change in Internal energy for process?
- Q.2 Given: $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$, $\Delta_r H^0 = -92.4\text{KJ.mol}^{-1}$. What is the standard enthalpy of formation of $NH_{3(g)}$.
- Q.3 Calculate entropy change in surroundings when 1.0 mol of $H_2O(l)$ is formed under standard conditions? Given $\Delta H^0 = -286\text{KJmol}^{-1}$.
- Q.4 Give relationship between entropy change and heat absorbed/evolved in a reversible reaction at temperature T.
- Q.5 What is spontaneous change? Give one example.

- Q.6 A real crystal has more entropy than an Ideal Crystal. Why?
- Q.7 Under what condition, the heat evolved/absorbed in a reaction is equal to its free energy change?
- Q.8 Predict the entropy change in-
- (i) A liquid crystallizes into solid
 - (ii) Temperature of a crystallized solid raised from 0K to 115K
- Q.9 What is bond energy? Why is it called enthalpy of atomization?
- Q.10 Calculate entropy change for the following process.



ANSWER FOR TWO MARKS QUESTIONS:

1. $q = 701\text{J}$, $w = 394\text{J}$, so $\Delta U = q + w = 701 - 394 = 307\text{J}$.
2. $\Delta_f H^\ominus \text{NH}_{3(g)} = -\frac{92.4}{2} = 46.2\text{KJ.mol}^{-1}$
3. $q_{(\text{rev.})} = -\Delta H^\ominus = -286 \text{ KJmol}^{-1} = 286000\text{Jmol}^{-1}$
- $$\Delta S = \frac{q_{(\text{rev.})}}{T} = \frac{286000 \text{ J.mol}^{-1}}{298 \text{ K}} = 959 \text{ J.K}^{-1}\text{mol}^{-1}$$
4. $\Delta S = \frac{q_{(\text{rev.})}}{T}$
5. A process which can take place of its own or initiate under some condition.
eg. Common salt dissolve in water of its own.
6. A real crystal has some disorder due to presence of defects in their structural arrangement, and Ideal crystal does not have any disorder.
7. In $\Delta G = \Delta H - T \cdot \Delta S$, when reaction is carried out at 0K or $\Delta S = 0$, then $\Delta G = \Delta H$.

8. (i) Entropy decreases b/c molecules attain an ordered state.
(ii) entropy increase b/c from 0K to 115K particles begin to move.
9. It is the amount of energy required to dissociate one mole of bonds present b/w atoms in gas phase. As molecules dissociates into atoms in gas phase so bond energy of diatomic molecules is called enthalpy of atomization.
10. $\text{H}_2\text{O}_{(\text{s})} \rightleftharpoons \text{H}_2\text{O}_{(\text{l})}$ at 0°C , $\Delta_{\text{fus}}\text{H} = 6\text{KJ mol}^{-1}$
 $= 6000\text{J mol}^{-1}$

$$\Delta T_f = 0^\circ\text{C} = 0 + 273 = 273\text{K}$$

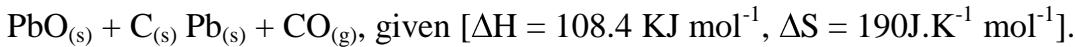
$$\text{Do } \Delta_{\text{fus}}\text{S} = \frac{\Delta_{\text{fus}}\text{H}}{T} = \frac{6000 \text{ J.mol}^{-1}}{273 \text{ K}} = 21.98 \text{ J.K}^{-1}\text{mol}^{-1}$$

THREE MARKS QUESTIONS:

- Q.1 For oxidation of iron, $4\text{Fe}_{(\text{s})} + 3\text{O}_{2(\text{g})} \rightarrow 2\text{Fe}_{2\text{O}}_{3(\text{s})}$
 ΔS is $-549.4\text{J.K}^{-1}\text{ mol}^{-1}$, at 298K. Inspite of -ve entropy change of this reaction, Why the reaction is spontaneous? ($\Delta_r\text{H}^0 = -1648 \times 10^3 \text{ J.mol}^{-1}$)
- Q.2 Using the bond energy of $H_r = 435 \text{ KJ mol}^{-1}$, $\text{Br}_2 = 192 \text{ KJ mol}^{-1}$, $\text{HBr} = 368 \text{ KJ mol}^{-1}$. Calculate enthalpy change for the reaction $\text{H}_{2(\text{g})} + \text{Br}_{2(\text{g})} \rightarrow 2\text{HBr}_{(\text{g})}$
- Q.3 Enthalpies of formation of $\text{CO}_{(\text{g})}$, $\text{CO}_{2(\text{g})}$, $\text{N}_2\text{O}_{(\text{g})}$ and $\text{N}_2\text{O}_{4(\text{g})}$ and -110 , -393 , 81 and 9.7 KJ mol^{-1} respectively. Find value $\Delta_r\text{H}$ for the reaction $\text{N}_2\text{O}_{4(\text{g})} + 3\text{CO}_{(\text{g})}$
- Q.4 For the reaction at 298K, $2\text{A} + \text{B} \rightarrow \text{C}$, $\Delta H = 400 \text{ KJ mol}^{-1}$, $\Delta S = 0.2 \text{ KJ mol}^{-1} \text{ K}^{-1}$. At what temperature will the reaction become spontaneous, considering ΔH , ΔS be constant at the temp.
- Q.5 The equilibrium constant for a reaction is 10. What will be the value of ΔG^0 ? $R = 8.314\text{J.K}^{-1}\text{mol}^{-1}$ $T = 300\text{K}$.
- Q.6 What do you understand by state function? Neither q nor w is a state function but $q + w$ is a state function? Explain.
- Q.7 Justify the following statements:

- (i) An endothermic reaction is always thermodynamically spontaneous.
- (ii) The entropy always increases on going from liquid to vapour state at any temperature T.

Q.8 Calculate the temperature above which the reduction reaction becomes spontaneous:



Q.9 From the data given below at 298K for the reaction:

$\text{CH}_{4(g)} + 2\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$ Calculate enthalpy of formation of $\text{CH}_{4(g)}$ at 298K. Given: $[\Delta_r H = -890.5 \text{ KJ}]$,

$$[\Delta_f H_{(\text{CO}_2)} = -393.5 \text{ KJ.mol}^{-1}, \Delta_f H_{(\text{H}_2\text{O})} = -286.0 \text{ KJ.mol}^{-1}]$$

Q.10 For the reaction $\text{NH}_4\text{Cl}_{(s)} \rightarrow \text{NH}_{3(g)} + \text{HCl}_{(g)}$ at 25^0C enthalpy change $\Delta H = 177 \text{ KJ.mol}^{-1}$ and $\Delta S = 285 \text{ J.K}^{-1} \text{ mol}^{-1}$. Calculate free energy change ΔG at 25^0C and predict whether the reaction is spontaneous or not.

ANSWER TO THREE MARKS QUESTIONS:

$$\text{Ans.1 } \Delta_{(\text{surr.})} = -\frac{\Delta_r H^0}{T} = -\frac{C - 1648 \times 10^3 \text{ J.mol}^{-1}}{298 \text{ K}} = 5530 \text{ JK}^{-1} \text{ mol}^{-1}.$$

$$\& \Delta S_{(\text{system})} = -549.4 \text{ QJK}^{-1} \text{ mol}^{-1}.$$

$$\Delta_r S_{(\text{total})} = 5530 - 5494 = 4980.6 \text{ J.K}^{-1} \text{ mol}^{-1}$$

Since $\Delta_r S_{(\text{total})}$ is +ve, so the reaction is spontaneous.

$$\text{Ans.2 } \Delta_r H^0 = \Sigma \text{bond enthalpies}_{(\text{rect.})} - \Sigma \text{bond enthalpies}_{(\text{prod.})}$$

$$= [H_{\text{H-H}}^0 + H_{\text{Br-Br}}^0] - [H_{\text{H-Br}}^0]$$

$$= [435 - 192] - [2 \times 368] \text{ KJ mol}^{-1}$$

$$= 627 - 736 = -109 \text{ KJ. Mol}^{-1} \text{ Ans.}$$

$$\text{Ans.3 } \Delta_r H = \Delta_f H^0_{(\text{prod.})} - \Delta_f H^0_{(\text{rect})}$$

$$= [H_f^0_{(\text{N}_2\text{O})} + 3\Delta_f H^0_{(\text{CO}_2)}] - [H_f^0_{(\text{N}_2\text{O}_4)} + 3\Delta_f H^0_{(\text{CO})}]$$

$$= [81 + 3(-393)] - [9.7 + (-110)]$$

$$= [81 + 1179] - [9.7 - 330] = -777.7 \text{ KJ}$$

Ans.4 $\Delta H = 400 \text{ KJ mol}^{-1}$, $\Delta S = 0.2 \text{ JK}^{-1} \text{ mol}^{-1}$.

$$\Delta G = \Delta H - T \cdot \Delta S$$

$$0 = 400 - 0.2 \times T \quad (\Delta G = 0 \text{ at equilibrium})$$

$$T = \frac{400}{0.2} = 2000 \text{ K}, \text{ so reaction will be spontaneous above } 2000 \text{ K.}$$

Ans.5 $\Delta_f G^0 = -2.303 RT \log K$

$$= -2.303 \times 8.314 \times 300 \times \log 10$$

$$= -19.147 \times 300 \times 1 = -5744.1 \text{ J}$$

$$\Delta_f G^0 = -5.7441 \text{ KJ.mol}^{-1}$$

Ans.6 The property whose value depends upon state of system and is independent of path. $q + w = \Delta U$, which is a state function as value of ΔU does not depends upon path.

Ans.7 (a) It is false, exothermic reaction is not always spontaneous. If $\Delta S = +ve$ and $T \cdot \Delta S > \Delta H$. The process will be non spontaneous even it. It is endothermic.

(b) The entropy of vapour is more than that of liquid, so entropy increases during vaporization.

Ans.8 $\Delta G = \Delta H - T \cdot \Delta S$, at equilibrium $\Delta G = 0, \Rightarrow \Delta H = T \cdot \Delta S$

$$\Rightarrow T = \frac{\Delta H}{\Delta S} = \frac{108.4 \times 10^3 \text{ J.mol}^{-1}}{190 \text{ J.K}^{-1} \text{ mol}^{-1}} = 570.526 \text{ K}$$

So the reaction will be spontaneous above 570.52K, as above this temperature ΔG will be -ve.

Ans.9 $\Delta_f H = \Delta_f H_{(CO_2)} + 2\Delta_f H_{CH_{4(g)}} - \Delta_f H_{(O_2)}$

$$-890.5 \text{ KJ} = -393.5 \text{ KJ} + 2v - 286 - \Delta H_f(CH_4) - O$$

$$= \Delta H_f(CH_4) = -75.0 \text{ KJ.mol}^{-1}.$$

$$= \Delta H_{f(CH_4)} = -75.0 \text{ KJ.mol}^{-1}.$$

Ans.10 $\Delta H = 177 \text{ KJ mol}^{-1}$, $\Delta S = 285 \text{ JK}^{-1} \text{ mol}^{-1}$

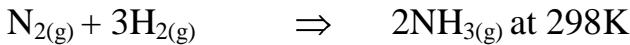
$$\Delta G = \Delta H - T \cdot \Delta S = 177 \text{ KJ} - \frac{298 \times 285}{1000} \text{ KJ}$$

$$= 177 \text{ KJ} - 84.93 \text{ KJ} = 92.07 \text{ KJ.mol}^{-1}.$$

Since ΔG is +ve, so the reaction is non spontaneous.

FIVE MARKS QUESTIONS:-

- Q.1 What is entropy? Why is the entropy of a substance taken as zero at 0K?
Calculate the $\Delta_r G$ for the reaction?



The value of equilibrium constant (K) is 6.6×10^5 , $R = 8.314 \text{ J.K}^{-1} \text{ mol}^{-1}$.

Ans: It is measure of randomness or disorder of system.

Because at 0 K there is complete order in the system.

$$\Delta G^0 = -2.303 RT \log K = -2.303 \times 8.314 \times 298 \times \log 6.6 \times 10^5$$

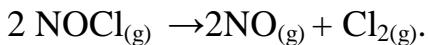
$$= -5705.8[\log 6.6 + \log 10^5]$$

$$= -5705.8[0.8195 + 5.0] = -5705.8 + 5.8195J$$

$$= -33204.903J$$

$$\Delta G^0 = -33.205 \text{ KJ mol}^{-1}$$

- Q.2 (i) What are extensive property and intensive properties?
(ii) Calculate the value of equilibrium constant (K) at 400K for



$$\Delta H^0 = 77.2 \text{ KJ.mol}^{-1}, \Delta S^0 = 122 \text{ J.K}^{-1} \text{ mol}^{-1} \text{ at } 400\text{K}, R = 8.314 \text{ J.K}^{-1} \text{ mol}^{-1}$$

Ans. (i) An **extensive property** is a property whose value depends on the quantity or size of matter present in the system. Those properties which do not depend on the quantity or size of matter present are known as **intensive properties**

$$(ii) \Delta H^0 = \Delta H^0 - T. \Delta S^0 = 77.2 \text{ KJ} - \frac{400 \times 122}{1000} \text{ KJ.mol}^{-1}$$

$$= 77.2 - 48.8 = 28.4 \text{ KJ mol}^{-1}$$

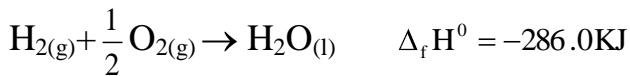
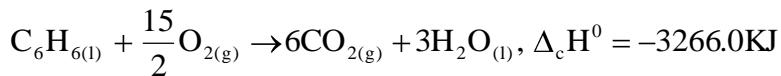
$$\text{and } \Delta G^0 = -2.303 RT \log K$$

$$28400 = -2.303 \times 8.314 \times 400 \log K$$

$$\log K = \frac{7.1}{2.303 \times 8.314} = -3.7081 = \bar{4.2919}K$$

$$K - \text{antilog } (\bar{4.2919}) = 1.95 \times 10^{-4} \text{ Ans.}$$

Q.3 Define standard enthalpy of formation. Calculate the enthalpy of formation of benzene from data



Ans. The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation.

$$\Delta_c H^0 = 6\Delta_f H_{(\text{CO}_2)}^0 + 3\Delta_f H_{(\text{H}_2\text{O})}^0 - \Delta_f H_{(\text{C}_6\text{H}_6)}^0 - \frac{15}{2}\Delta_f H_{(\text{O}_2)}^0$$

$$= -3266\text{KJ} = 6 \times -393.1 + 3 \times -286 - \Delta_f H_{(\text{C}_6\text{H}_6)}^0 - 0$$

$$= -3218 \text{ kJ/mol}$$

HOTS QUESTIONS

1. Why standard entropy of an elementary substance is not zero whereas standard enthalpy of formation is taken as zero?

Ans. A substance has a perfectly ordered arrangement only at absolute zero. Hence, entropy is zero only at absolute zero. Enthalpy of formation is the heat change involved in the formation of one mole of the substance from its elements. An element formed from it means no heat change.

2. The equilibrium constant for a reaction is one or more if ΔG° for it is less than zero. Explain

Ans. $-\Delta G^\circ = RT \ln K$, thus if ΔG° is less than zero. i.e., it is negative, then $\ln K$ will be positive and hence K will be greater than one.

3. Many thermodynamically feasible reactions do not occur under ordinary conditions. Why?

Ans. Under ordinary conditions, the average energy of the reactants may be less than threshold energy. They require some activation energy to initiate the reaction.

CHAPTER-7

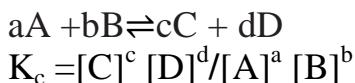
EQUILIBRIUM

- Equilibrium state- When rate of formation of a product in a process is in competition with rate of formation of reactants, the state is then named as “Equilibrium state” .

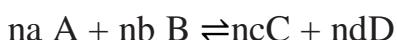
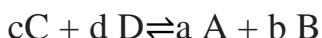
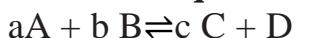
- Equilibrium in physical processes: $\text{solid} \rightleftharpoons \text{liquid} \rightleftharpoons \text{gas}$



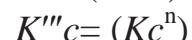
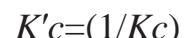
- Law of chemical equilibrium: At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the Equilibrium Law or Law of Chemical Equilibrium.



Chemical equation



Equilibrium constant



Concentrations or partial pressure of pure solids or liquids do not appear in the expression of the equilibrium constant. In the reaction,



- If $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse reaction). If $Q_c < K_c$, the reaction will proceed in the direction of the products (forward reaction)
- K_p is equilibrium constant in terms of partial pressure of gaseous reactants and products.
- K_c is equilibrium constant in terms of molar concentration of gaseous reactants and products.
- $K_p = K_c (RT)^{\Delta n}$ here R is gas constant, T is temperature at which the process is carried out & Δn is no. of moles of gaseous product minus no. of moles of gaseous reactants.
- If $K_c > 10^3$; K_c is very high i.e. the reaction proceeds nearly to completion.
- If $K_c < 10^{-3}$; K_c is very small i.e. the reaction proceeds rarely.
- If K_c is ranging in the range of 10^3 to 10^{-3} ; i.e. reactants and products are just in equilibrium.
- $\Delta G^0 = -RT \ln K$ or $\Delta G^0 = -2.303RT \log K$
- Factors affecting equilibrium constant:- temperature, pressure, catalyst and molar concentration of reactants and products.

- **Le Chatelier's principle**:- It states that a **change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.**
- Arrhenius acids are the substances that ionize in water to form H^+ .
- Arrhenius bases are the substances that ionize in water to form OH^- .
- Lewis acids are lone pair (of e-) acceptors while Lewis bases are lone pair donators.
- Proton donor are acids while proton acceptors are bases(Bronsted-Lowry concept).
- The acid-base pair that differs only by one proton is called a **conjugate acid-base pair**. If Brönsted acid is a strong acid then **its conjugate base is a weak base and viceversa**.
- **Ionic product of water**. $K_w = [\text{H}^+][\text{OH}^-]$
- **pH = -log [H⁺]**; here $[\text{H}^+]$ is molar concentration of hydrogen ion.
- **pH + pOH = 14**
- **pK_a + pK_b = 14**
- **$\text{K}_a \times \text{K}_b = K_w = \text{ionic product of water} = 1 \times 10^{-14}$**
- **Buffer solution** :The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.
- **common ion effect**: It can be defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium.
- **Hydrolysis of Salts**: process of interaction between water and cations/anions or both of salts is called hydrolysis.
- The cations (e.g., Na^+ , K^+ , Ca^{2+} , Ba^{2+} , etc.) of strong bases and anions (e.g., Cl^- , Br^- , NO_3^- , ClO_4^- etc.) of strong acids simply get hydrated but do not hydrolyse, and therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7.
- Salts of weak acid and strong base e.g., CH_3COONa are basic in nature.
- Salts of strong acid and weak base e.g., NH_4Cl , are acidic
- Salts of weak acid and weak base, e.g., $\text{CH}_3\text{COONH}_4$. The pH is determined by the formula $\text{pH} = 7 + \frac{1}{2} (\text{pK}_a - \text{pK}_b)$
- **Solubility product**- product of the molar concentrations of the ions in a saturated solution, each concentration term raised to the power equal to the no. of ions produced.

ONE MARK QUESTIONS

Q.1. Mention the factors that affect equilibrium constant.

Ans. Temperature, pressure, catalyst and molar concentration of reactants and products.

Q.2. What is ionic products of water?

Ans. $K_w = [H^+] [OH^-]$

Q.3. Write conjugate acids of H_2O & NH_3 .

Ans. H_3O^+ & NH_4^+ .

Q.4. Define Arrhenius acids.

Ans. Arrhenius acids are the substances that ionize in water to form H^+ .

Q.5. Define the term degree of ionization.

Ans. Extent up to which an acid/base/salt ionize to form ions.

Q.6. What are Buffer solutions?

Ans. The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.

Q.7. Write K_c for the gaseous reaction- $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Ans. $K_c = [NH_3]^2 / [N_2] [H_2]^3$

Q.8. Out of H_2O & H_3O^+ which is stronger acid?

Ans. H_3O^+ .

Q.9. What is common ion effect?

Ans. Shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium.

Q.10. Write relationship between K_p and K_c for the gaseous reaction - $N_2 + O_2 \rightleftharpoons 2NO$

Ans. $K_p = K_c$ as Δn is zero for the above said reaction.

TWO MARKS QUESTIONS

1. What is effect of catalyst on equilibrium constant ‘ K_c ’?

Ans . A catalyst does not affect equilibrium constant because it speeds up both forward and backward reactions to the same extent.

2. State Le Chatelier’s principle.

Ans. It states that a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.

3. What is meant by conjugate acid –base pairs? Explain.

Ans:-
$$\begin{array}{ccccccc} & H_2O & + & HCl & \rightleftharpoons & H_3O^+ & + & Cl^- \\ & \text{base} & & \text{acid} & & \text{conjugate acid} & & \text{conjugate base} \end{array}$$

4. Classify the following bases as strong and weak bases: NaHCO_3 , NaOH , KOH , $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$.

Ans:-strong base NaOH , KOH ; weak bases NaHCO_3 , $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$.

5. The concentration of hydrogen ion in a sample of soft drink is $3.8 \times 10^{-3}\text{M}$. What is its pH?

$$\text{Ans:}-\text{pH} = -\log[3.8 \times 10^{-3}]$$

$$= -\{\log[3.8] + \log[10^{-3}]\}$$

$$= -\{(0.58) + (-3.0)\} = -\{-2.42\} = 2.42$$

Therefore, the pH of the soft drink is 2.42 and it is acidic.

6. The species: H_2O , HCO_3^- , HSO_4^- and NH_3 can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and conjugate base.

Ans:-

| Species | Conjugate acid | Conjugate base |
|----------------------|-------------------------|--------------------|
| H_2O | H_3O^+ | OH^- |
| HCO_3^- | H_2CO_3 | CO_3^{2-} |
| HSO_4^- | H_2SO_4 | SO_4^{2-} |
| NH_3 | NH_4^+ | NH_2^- |

7. Explain Lewis acids and bases with suitable examples.

Ans:- Lewis acids are lone pair (of e-) acceptors while Lewis bases are lone pair donors.

AlCl_3 is a Lewis acid while NH_3 is a Lewis base.

8. What is difference between alkali and bases? Give examples.

Ans:- An alkali is a water soluble base. All the alkalis are bases but all the bases are not alkali. Ex- NaOH is an alkali/base.

$\text{Ca}(\text{OH})_2$ is a base but not an alkali.

9. Explain homogeneous and heterogeneous equilibrium giving examples.

Ans:- If all the reactants and products present in an equilibrium mixture are in same phase \rightarrow homogeneous equilibrium.

If all the reactants and products present in an equilibrium mixture are in different phase \rightarrow heterogeneous equilibrium.



THREE MARK QUESTIONS

1. The pH of some common substances is given below. Classify the substances as acidic/basic

| Name of fluid | pH |
|------------------|-----|
| Lime water | 10 |
| Milk of magnesia | 10 |
| Human saliva | 6.4 |
| Lemon juice | 2.2 |
| Sea water | 7.8 |
| Vinegar | 3 |
| milk | 6.8 |

Ans.: - acidic-Human saliva, Lemon juice, milk, vinegar

Basic- Lime water, sea water, milk of magnesia.

2. Explain general characteristics of acids and bases.

Ans.: - Most of the acids taste sour. Acids are known to turn blue litmus paper into red and liberate dihydrogen on reacting with some metals.

Bases are known to turn red litmus paper blue, taste bitter and feel soapy.

3. Water is amphoteric in nature. Explain.

Ans.: - Water can react with acid as well as base



4. Describe the effect of :

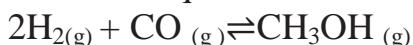
a) addition of H_2

b) addition of CH_3OH

c) removal of CO

d) removal of CH_3OH

on the equilibrium of the reaction:



Ans.: - a) addition of H_2

equilibrium will shift on RHS

b) addition of CH_3OH

equilibrium will shift on LHS

c) removal of CO

equilibrium will shift on LHS

d) removal of CH_3OH

equilibrium will shift on RHS

5. Classify the following species into Lewis acids and Lewis bases and show how these act as such:

(a) HO^- (b) F^- (c) H^+ (d) BCl_3

Solution

(a) Hydroxyl ion is a Lewis base as it can donate an electron lone pair ($:\text{OH}^-$).

(b) Fluoride ion acts as a Lewis base as it can donate any one of its four electron lone pairs.

- (c) A proton is a Lewis acid as it can accept a lone pair of electrons from bases like hydroxyl ion and fluoride ion.
- (d) BCl_3 acts as a Lewis acid as it can accept a lone pair of electrons from species like ammonia or amino molecules.
- 6.** For the equilibrium, $2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g)$ the value of the equilibrium constant, K_c is 3.75×10^{-6} at 1069 K. Calculate the K_p for the reaction at this temperature?

Solution

We know that, $K_p = K_c (RT)^{\Delta n}$

For the above reaction, $\Delta n = (2+1) - 2 = 1$

$$K_p = 3.75 \times 10^{-6} (0.0831 \times 1069)$$

$$K_p = 0.033.$$

- 7.** Hydrolysis of sucrose gives, Sucrose + $\text{H}_2\text{O} \rightarrow$ Glucose + Fructose
Equilibrium constant K_c for the reaction is 2×10^{13} at 300K. Calculate ΔG^0 at 300K.

Solution

$$\Delta G^0 = -RT \ln K_c$$

$$\Delta G^0 = -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K} \times \ln(2 \times 10^{13})$$

$$\Delta G^0 = -7.64 \times 10^4 \text{ J mol}^{-1}$$

- 8.** Explain the following :

(i) Common ion effect (ii) solubility products (iii) pH

Ans. (i) Suppression of ionization of weak electrolyte by adding a strong electrolyte having an ion common.

(ii) Product of the molar concentrations of the ions in a saturated solution, each concentration term raised to the power equal to the no. of ions produced.

(iii) Negative logarithm of hydrogen ion concentration.

- 9.** The values of K_{sp} of two sparingly soluble salts Ni(OH)_2 and AgCN are 2.0×10^{-15} and 6×10^{-17} respectively. Which salt is more soluble? Explain.

Solution



$$K_{sp} = [\text{Ag}^+][\text{CN}^-] = 6 \times 10^{-17}$$



$$K_{sp} = [\text{Ni}^{2+}][\text{OH}^-]^2 = 2 \times 10^{-15}$$

Let $[\text{Ag}^+] = S_1$, then $[\text{CN}^-] = S_1$

Let $[\text{Ni}^{2+}] = S_2$, then $[\text{OH}^-] = 2S_2$

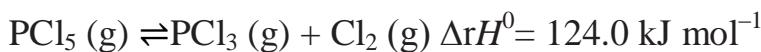
$$S_1^2 = 6 \times 10^{-17}, S_1 = 7.8 \times 10^{-9}$$

$$(S_2)(2S_2)^2 = 2 \times 10^{-15}, S_2 = 0.58 \times 10^{-4}$$

Ni(OH)_2 is more soluble than AgCN .

FIVE MARKS QUESTIONS

1. At 473 K, equilibrium constant K_c for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3} . If decomposition is depicted as,



- a) Write an expression for K_c for the reaction.
 b) What is the value of K_c for the reverse reaction at the same temperature?

c) what would be the effect on K_c if (i) more PCl_5 is added (ii) pressure is increased (iii) the temperature is increased ?

Ans: (a)
$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

- (b) 120.48
 (c) (i) equilibrium will shift on RHS
 (ii) equilibrium will shift on LHS
 (iii) equilibrium will shift on RHS

2. Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction: $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$
 (a) Write an expression for K_p for the above reaction.
 (b) How will the values of K_p and composition of equilibrium mixture be affected by (i) increasing the pressure (ii) increasing the temperature (iii) using a catalyst?

Ans. (a) $K_p = p(\text{CO}) \cdot p(\text{H}_2)^3 / p(\text{CH}_4) \cdot p(\text{H}_2\text{O})$

- (b) (i) value of K_p will not change, equilibrium will shift in backward direction.
 (ii) Value of K_p will increase and reaction will proceed in forward direction.
 (iii) no effect.

3. What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species: HNO_2 , CN^- , HClO_4 , F^- , OH^- , CO_3^{2-} , and S^{2-}

Ans. The acid-base pair that differs only by one proton is called a conjugate acid-base pair

| Species | Conjugate acid/base |
|--------------------|----------------------|
| HNO_2 | NO_2^- |
| CN^- | HCN |
| HClO_4 | ClO_4^- |
| F^- | HF |
| OH^- | H_2O |
| CO_3^{2-} | HCO_3^{2-} |

S^{2-}

HS^-

HOTS QUESTIONS

1. The value of K_c for the reaction $2A \rightleftharpoons B + C$ is 2×10^{-3} . At a given time, the composition of reaction mixture is $[A] = [B] = [C] = 3 \times 10^{-4} M$. In which direction the reaction will proceed?

Solution

For the reaction the reaction quotient Q_c is given by, $Q_c = [B][C]/[A]^2$
as $[A] = [B] = [C] = 3 \times 10^{-4} M$

$$Q_c = (3 \times 10^{-4})(3 \times 10^{-4}) / (3 \times 10^{-4})^2 = 1$$

as $Q_c > K_c$ so the reaction will proceed in the reverse direction.

2. PCl_5 , PCl_3 and Cl_2 are at equilibrium at 500 K and having concentration 1.59M PCl_3 , 1.59M Cl_2 and 1.41 M PCl_5 . Calculate K_c for the reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Solution

The equilibrium constant K_c for the above reaction can be written as,

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= (1.59)^2 / 1.41 = 1.79$$

3. Why is ammonia termed as a base though it does not contain OH^- ions?

Ans. Ammonia is termed as a base on the basis of Lewis concept it can donate a lone pair of electrons.

CHAPTER-8 REDOX REACTIONS

| <u>oxidation</u> | <u>reduction</u> |
|---|---|
| 1. Addition of oxygen | 1. Removal of oxygen |
| 2. Removal of hydrogen | 2. Addition of hydrogen |
| 3. Addition of an electronegative element | 3. Removal of an electronegative element |
| 4. Removal of an electropositive element | 4. Addition of an electropositive element |
| 5. Loss of electron | 5. Gain of electron |

Oxidation number denotes the oxidation state of an element in a compound ascertained according to a set of rules formulated on the basis that an electron in a covalent bond belongs entirely to more electronegative element.

Calculation of oxidation number-

1. O. S. of all the elements in their elemental form (in standard state) is taken as zero. O. S. of elements in Cl_2 , F_2 , O_2 , P_4 , O_3 , Fe(s) , H_2 , N_2 , C(graphite) is zero.
2. Common O. S. of elements of group one (1^{st}) is one. Common O. S. of elements of group two (2^{nd}) is two.
3. For ions composed of only one atom, the oxidation number is equal to the charge on the ion.
4. The oxidation number of oxygen in most compounds is -2 . While in peroxides (e.g., H_2O_2 , Na_2O_2), each oxygen atom is assigned an oxidation number of -1 , in superoxides (e.g., KO_2 , RbO_2) each oxygen atom is assigned an oxidation number of $-(\frac{1}{2})$.
5. In oxygendifluoride (OF_2) and dioxygendifluoride (O_2F_2), the oxygen is assigned an oxidation number of $+2$ and $+1$, respectively.
6. The oxidation number of hydrogen is $+1$ but in metal hydride its oxidation no. is -1 .
7. In all its compounds, fluorine has an oxidation number of -1 .
8. The algebraic sum of the oxidation numbers of all the atoms in a compound must be zero.
9. In polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion must equal the charge on the ion.

Stock notation: the oxidation number is expressed by putting a Roman numeral representing the oxidation number in parenthesis after the symbol of the metal in the molecular formula. Thus aurous chloride and auric chloride are written as Au(I)Cl and Au(III)Cl_3 . Similarly, stannous chloride and stannic chloride are written as Sn(II)Cl_2 and Sn(IV)Cl_4 .

Oxidation: An increase in the oxidation number

Reduction: A decrease in the oxidation number

Oxidising agent: A reagent which can increase the oxidation number of an element in a given substance. These reagents are called as **oxidants** also.

Reducing agent: A reagent which lowers the oxidation number of an element in a given substance. These reagents are also called as **reductants**.

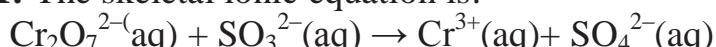
Redox reactions: Reactions which involve change in oxidation number of the interacting species

Balancing of redox reactions:

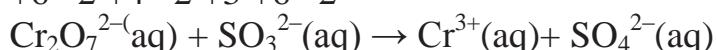
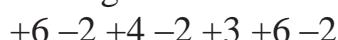
Oxidation Number Method:

Write the net ionic equation for the reaction of potassium dichromate(VI), $\text{K}_2\text{Cr}_2\text{O}_7$ with sodium sulphite, Na_2SO_3 , in an acid solution to give chromium(III) ion and the sulphate ion.

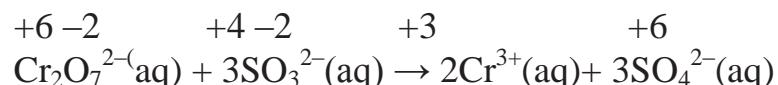
Step 1: The skeletal ionic equation is:



Step 2: Assign oxidation numbers for Cr and S



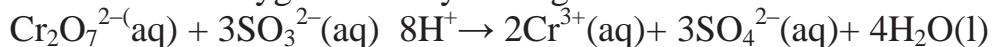
Step 3: Calculate the increase and decrease of oxidation number, and make them equal:



Step 4: Balance the charge by adding H^+ as the reaction occurs in the acidic medium,



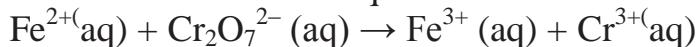
Step 5: Balance the oxygen atom by adding water molecule.



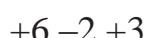
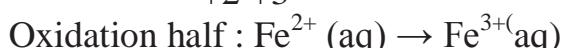
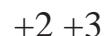
Half Reaction Method

balance the equation showing the oxidation of Fe^{2+} ions to Fe^{3+} ions by dichromate ions ($\text{Cr}_2\text{O}_7^{2-}$) in acidic medium, wherein, $\text{Cr}_2\text{O}_7^{2-}$ ions are reduced to Cr^{3+} ions.

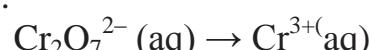
Step 1: Produce unbalanced equation for the reaction in ionic form :



Step 2: Separate the equation into half reactions:

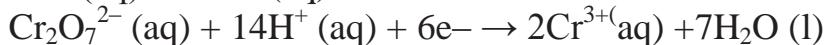


Step 3: Balance the atoms other than O and H in each half reaction individually.

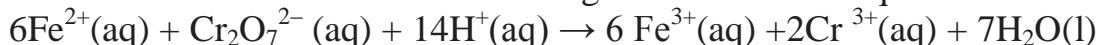


Step 4: For reactions occurring in acidic medium, add H_2O to balance O atoms and H^+ to balance H atoms. $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+ \rightarrow \text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$

Step 5: Add electrons to one side of the half-reaction to balance the charges. If needed, make the number of electrons equal in the two half-reactions by multiplying one or both half-reactions by appropriate coefficients.



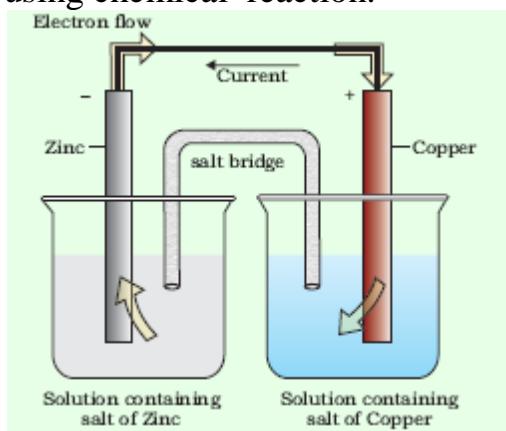
Step 6: We add the two half-reactions to achieve the overall reaction and cancel the electrons on each side. This gives the net ionic equation as :



A **redox couple** is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half-reaction.

Represented as Zn^{2+}/Zn and Cu^{2+}/Cu .

- ❖ Electrochemical cells are the devices which are used to get electric current by using chemical reaction.



Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.

The potential associated with each electrode is known as **electrode potential**. If the concentration of each species taking part in the electrode reaction is unity (if any gas appears in the electrode reaction, it is confined to 1 atmospheric pressure) and further the reaction is carried out at 298K, then the potential of each electrode is said to be the **Standard Electrode Potential**.

- SHE is used to measure electrode potential and its standard electrode potential is taken as 0.00 V.

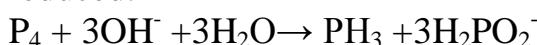
ONE MARK QUESTIONS

1. Define oxidation and reduction in terms of oxidation number.

Ans Increase in Oxidation Number is Oxidation and decrease in Oxidation Number is called reduction.

2. What is meant by disproportionation? Give one example.

Ans : In a disproportionation reaction an element simultaneously oxidized and reduced.

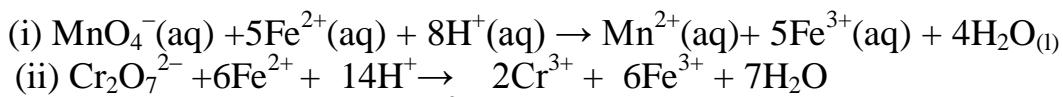


3. What is O.N. of sulphur in H_2SO_4 ? Ans: +6

4. Identify the central atom in the following and predict their O.S.
 HNO_3
 Ans: central atom:- N; O.S. +5
5. Out of Zn and Cu which is more reactive?
 Ans: Zn.
6. What is galvanization?
 Ans: Coating of a less reactive metal with a more reactive metal e.g.- coating of iron surface with Zn to prevent rusting of iron.
7. How is standard cell potential calculated using standard electrode potential?
 Ans: $E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$
8. What is O.S. of oxygen in H_2O_2 ?
 Ans: - -1.
9. The formation of sodium chloride from gaseous sodium and gaseous chloride is a redox process justify.
 Ans: Na atom get oxidized and Cl is reduced.

TWO MARKS QUESTIONS

1. Write the balanced redox reaction .
 (I) $\text{MnO}_4^-(\text{aq}) + \text{Fe}^{2+}(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + \text{Fe}^{3+}(\text{aq})$ [acidic medium]
 (II) $\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{2+} \rightarrow \text{Cr}^{3+} + \text{Fe}^{3+}$ [Acidic medium]
- Ans:- (i) $\text{MnO}_4^-(\text{aq}) + 5\text{Fe}^{2+}(\text{aq}) + 8\text{H}^+(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + 5\text{Fe}^{3+}(\text{aq}) + 4\text{H}_2\text{O}_{(\text{l})}$
 (ii) $\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$
2. Identify the strongest & weakest reducing agent from the following metals:
.Zn, Cu, Na, Ag, Sn
 Ans: Strongest reducing agent: Na, weakest reducing agent: Ag.
3. Determine the oxidation no. of all the atoms in the following oxidants: KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ and KClO_4
 Ans :
 In KMnO_4 K = +1, Mn = +7, O = -2
 In $\text{K}_2\text{Cr}_2\text{O}_7$ K = +1, Cr = +6, O = -2
 In KClO_4 K = +1, Cl = +7, O = -2
4. Determine the oxidation no. of all the atoms in the following species: Na_2O_2 and OF_2 .
 Ans: In Na_2O_2 Na = +1, O = -1
 In OF_2 , F = -1, O = +2
5. Is it possible to store :
(i) H_2SO_4 in Al container? (ii) CuSO_4 solution in Zn vessel?
 Ans : (i) yes. (ii) No.
6. Calculate the standard e.m.f. of the cell formed by the combination of $\text{Zn}/\text{Zn}^{2+} \parallel \text{Cu}^{2+}/\text{Cu}$.
 Solution- : $E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$
 $= 0.34 - (-0.76) = 1.10\text{V}$.
7. Identify the oxidizing and reducing agents in the following equations:



Ans : (i) O.A. = MnO_4^- ; R.A. = Fe^{2+}

(ii) O.A. = $\text{Cr}_2\text{O}_7^{2-}$; R.A. = Fe^{2+}

8. Predict all the possible oxidation states of Cl in its compounds.

Ans:- 0, -1, +1, +3, +5, +7

9. Formulate possible compounds of 'Cl' in its O.S.is: 0, -1, +1, +3, +5, +7

Ans: Cl_2 , HCl , HOCl , HOClO , HOClO_2 , HOClO_3 respectively.

10. List three measures used to prevent rusting of iron.

Ans: (i) galvanization(coating iron by a more reactive metal)

(ii) greasing/oiling

(iii) painting.

THREE MARK QUESTIONS

1. Write short notes on :

(a) Electrochemical series (b) redox reactions (c) oxidizing agents

Ans :(a) Electrochemical series :- arrangement of metals(non-metals also) in increasing order of their reducing power or vice versa.

(b) Reactions in which both Oxidation and reduction take place simultaneously are REDOX REACTIONS.

(c) oxidizing agents : chemical specie which can oxidize the other one or can reduce itself.

2. Calculate O. S. of sulphur in the following oxoacids of 'S' :

H_2SO_4 , H_2SO_3 , $\text{H}_2\text{S}_2\text{O}_8$ and $\text{H}_2\text{S}_2\text{O}_7$

Ans : +6, +4, +6 and +6 respectively.

(calculate by considering x of 'S' and taking +1 of H, -2 of "O" and -1 of "O" in peroxide bond.)

3. Explain role of salt bridge in Daniell cell.

Ans : (a) it completes the electric circuit in the cell.

(b) it maintains the electric neutrality in the cell.

4. Account for the followings :

(i) sulphur exhibits variable oxidation states.

Ans. Due to the presence of vacant 'd' orbitals in 'S'

(ii) Fluorine exhibits only -1 O.S.

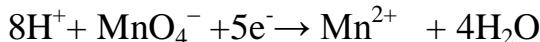
Ans . It is most electronegative element

(iii) oxygen can't extend its valency from 2.

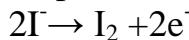
Ans. Small size/unavailability of vacant 'd' orbitals in O

5. Balance the equation $\text{MnO}_4^- + \text{I}^- \rightarrow \text{Mn}^{2+} + \text{I}_2 + \text{H}_2\text{O}$ by ion electron method in acidic medium.

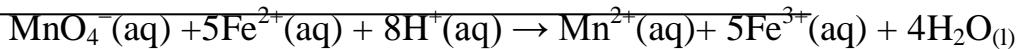
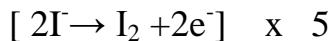
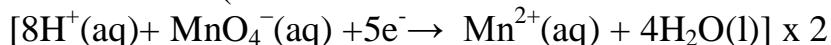
Ans : Step-I Balancing of reduction half reaction by adding protons and electrons on LHS and more water molecules on RHS:



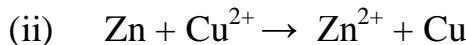
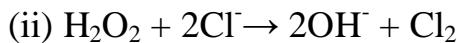
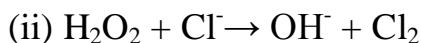
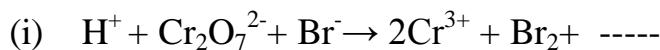
Step-II Balancing of oxidation half reaction by adding electrons on RHS:



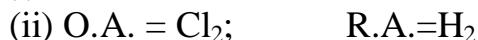
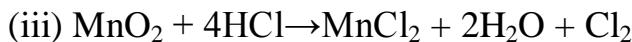
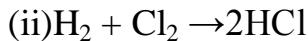
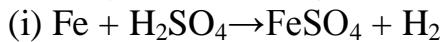
Step-III To multiply the OHR by 5; RHR by 2 and to add OH & RH reactions to get overall redox reaction(cancellation of electrons of RH & OH reactions):



6. complete and balance the following equations:



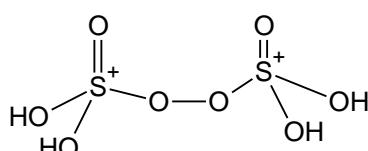
7. Identify the oxidizing and reducing agents in the following equations:



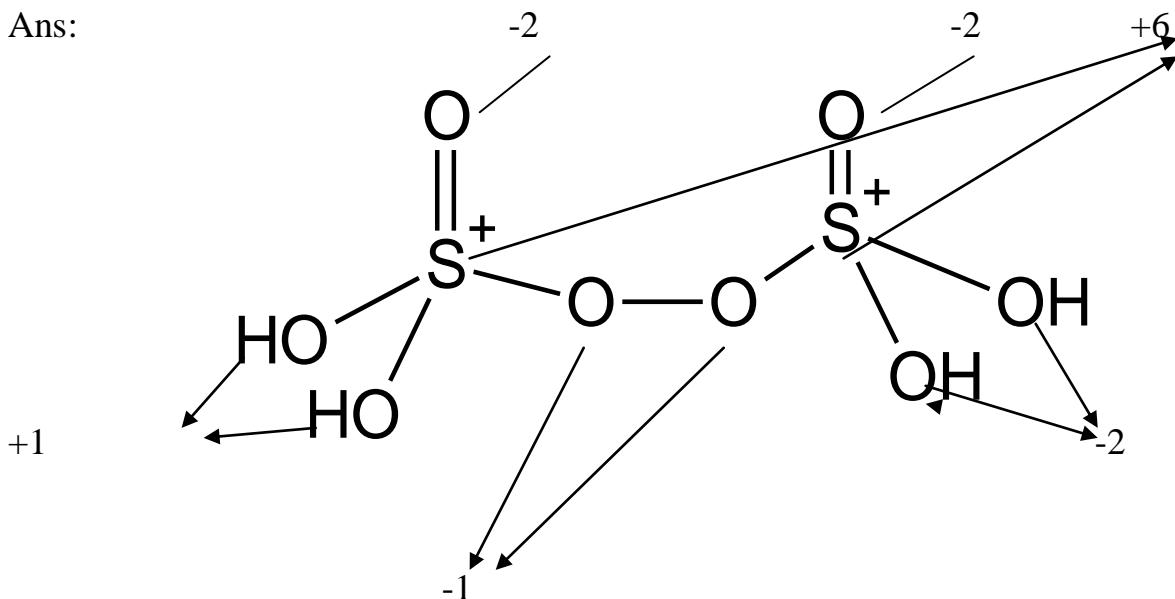
8. Arrange the following in increasing order of their reducing power:



9. Indicate O.S. of each atom present in given structure of peroxodisulphuric acid



Ans:



10.What is SHE? What is its use?

Ans :Standard Hydrogen Electrode (SHE) has been selected to have zero standard potential at all temperatures. It consists of a platinum foil coated with platinum black (finely divided platinum) dipping partially into an aqueous solution in which the activity (approximate concentration 1M) of hydrogen ion is unity and hydrogen gas is bubbled through the solution at 1 bar pressure. The potential of the other half cell is measured by constructing a cell in which reference electrode is standard hydrogen electrode. The potential of the other half cell is equal to the potential of the cell.

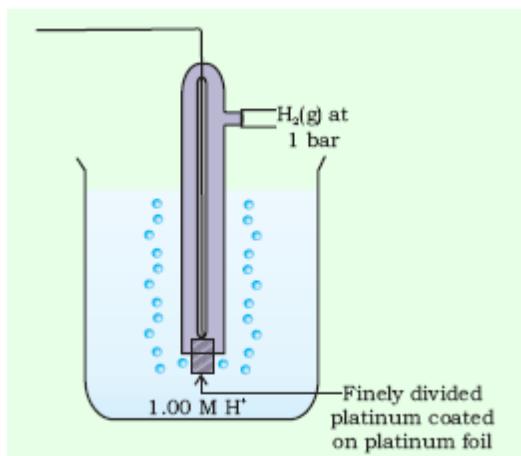


Fig: SHE

HOTS QUESTIONS

1. Is rusting of iron an electrochemical phenomenon? How ?explain.

Ans : Yes. Rusting of iron is an electrochemical phenomenon because this is possible due to formation of a small electrochemical cell over rough surface of iron and the following redox reaction takes place there in that cell-

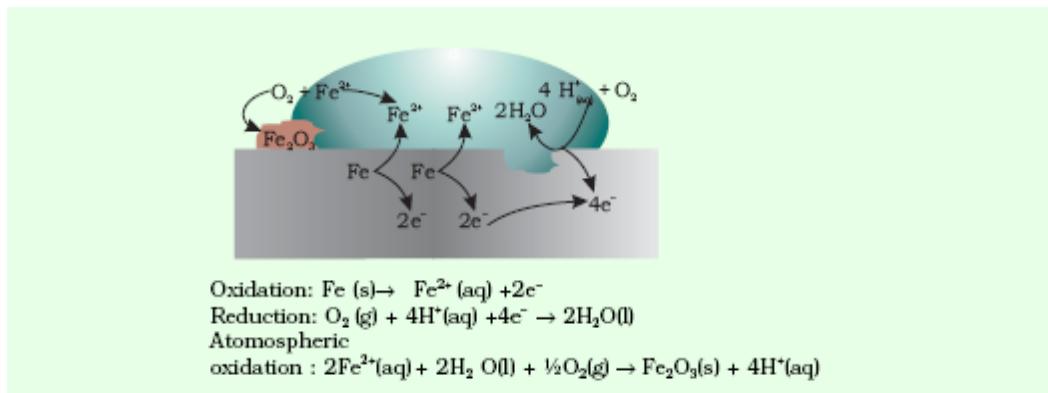
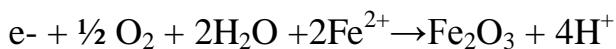
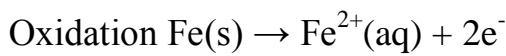


Fig. 5.14 Corrosion of iron in atmosphere.

2. We expand crores of Rupees and even thousands of lives every year due to corrosion. How can be preventing it. Explain.

Ans : (i) By Galvanization: Coating of a less reactive metal with a more reactive metal e.g.- coating of iron surface with Zn to prevent rusting of iron.

(ii) By greasing /oiling (to keep away the object from the contact of air & moisture.)

(iii) By painting (to keep away the object from the contact of air & moisture.)

CHAPTER 9

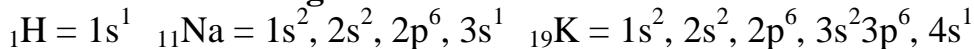
HYDROGEN

★ Position of Hydrogen in Periodic Table

- Lightest element known having atomic number 1.
- Dihydrogen
- It resembles both alkali metals and halogens and therefore, its position is anomalous.
- In modern periodic table it is located separately

★ Resemblance with alkali metals:-

1. Electronic configuration



2. Electropositive character: H^+ , Na^+ , K^+ etc.

3. Oxidation state: +1

4. Combination with electronegative elements: form binary compounds with electronegative elements like alkali metals.

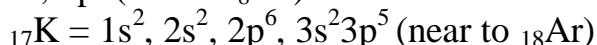
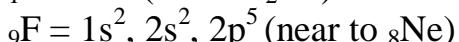
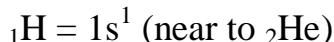
Halides: HCl , NaCl , KCle etc

Sulphides: H_2S Na_2S , K_2S etc

★ Resemblance with halogens:-

1. Electronic configuration:

Both contain one electron less than the nearest noble gas configuration



2. Non-metallic character: like halogens, hydrogen is non-metallic in nature.

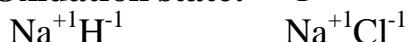
3. Atomicity: Diatomic molecules.

4. Formation of similar types of compounds:

i. Halides: CCl_4 , SiCl_4 , GeCl_4

ii. Hydrides: CH_4 , SiH_4 , GeH_4

5. Oxidation state: -1



★ Difference from alkali metals:-

1) **Ionization enthalpy:** - the ionization enthalpy of hydrogen is very high in comparison to alkali metals.

2) **Non-metallic character:** alkali metals are typical metals while hydrogen is non-metal

3) **Atomicity:** hydrogen is diatomic while alkali metals are monoatomic.

4) **Nature of compounds:** the compounds of hydrogen are predominantly covalent while those of alkali metals are ionic. For example: HCl is covalent while NaCl is ionic.

The oxides of alkali metals are basic while hydrogen oxide is neutral.

★Difference from halogens:-

- 1) **Less tendency for hydride formation:** Hydrogen has less tendency to take up electron to form hydride ion (H^-) as compared to the halogens which form halide ions (X^-) very easily.
- 2) **Absence of unshared pairs of electrons :**
- 3) **Nature of oxides:** The oxides of halogens are acidic while hydrogen oxide is neutral.

★ Occurrence of Hydrogen:

- Hydrogen, the most abundant element in the universe and the third most abundant on the surface of the globe, is being visualised as the major future source of energy

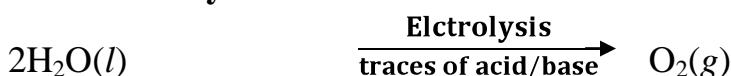
★Isotopes of hydrogen:-

| S.N. | Property | Protium | Deuterium | Tritium |
|------|-----------------------|-----------------|-----------------|--|
| 1 | Relative abundance | 99.985 % | 0.015 % | $10^{-15}\%$ |
| 2 | Relative atomic mass | 1.007825 | 2.014102 | 3.016 |
| 3 | Radioactive stability | Non-radioactive | Non-radioactive | Radioactive $t_{1/2} = 12.334$ yrs |

★ Preparation:

★Methods for commercial production of dihydrogen

1. Electrolysis of water

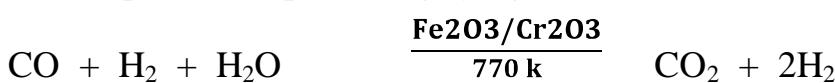


- The hydrogen prepared by this method is of very high purity. However, this method is not commonly used because it is very expensive. This method can be used only at those places where the electricity is cheap.

2. By the reaction of steam on coke :-



- Since the mixture of CO and H_2 is used for the synthesis of methanol and a number of hydrocarbons, it is also called synthesis gas or syn gas.
- The process of producing syn gas from coal or coke is called coal gasification.



Water gas steam

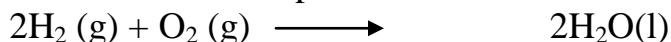
- This reaction is called water gas shift reaction.

★Properties of Hydrogen:-

☆Physical Properties:-

- 1) It is slightly soluble in water (about 2 %)
- 2) It is highly combustible and therefore should be handled carefully.
- 3) It lightest substance. The weight of one litre hydrogen at NTP is only 0.0899 g.
☆Chemical properties:-Not very reactive due to high bond dissociation energy (435.88 kJ mol⁻¹ at 298.2 K)

(i) **Combustion:** - It burns with pale blue flame

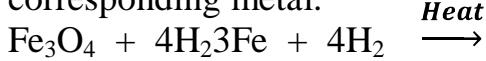


(ii) **Reaction with metals:**-Reactive metals like Na, K, Ca, Li and form hydrides.

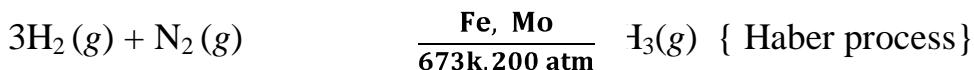


➤ Metals like Pt, Pd, Ni (elements of d block) form interstitial hydrides by absorbing large volume of hydrogen. Such hydrogen is called ‘occluded’ hydrogen and this property of adsorption of a gas by a metal is called occlusion.

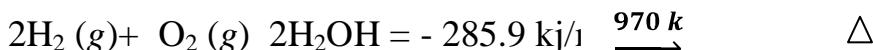
(iii) **Reaction with metal oxides:**-Hydrogen reduces oxides of less active metals to corresponding metal.



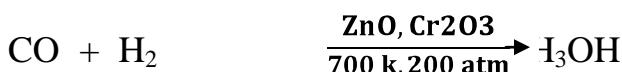
(iv) **Reaction with non-metals:**-



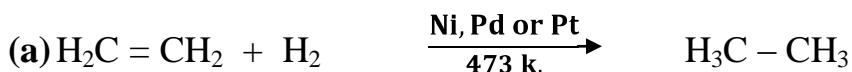
$$\Delta H = -92.6 \text{ kJ/mole}$$



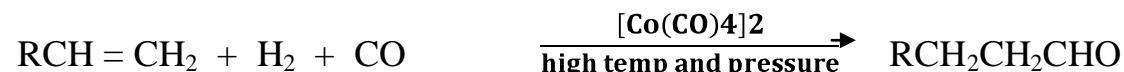
(v) **Reaction with carbon monoxide:**-



(vi) **Reaction with unsaturated Hydrocarbons:**-



(b) **Hydroformylation of olefins to aldehydes:** Hydroformilation or Oxo process



(c) **Hydrogenation of oils:**-Vegetable oils are polyunsaturated in nature. The C=C bonds in oils can easily undergo oxidation and the oil becomes rancid i.e.,

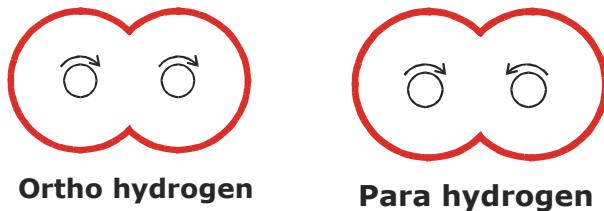
unpleasant in taste. Hydrogenation reduces the number of double bonds but completely.



★Uses of Hydrogen:-it is used ..

1. as a reducing agent.
2. In the manufacture of vanaspati fat, ammonia, metal hydrides, methanol, fertilizers such as urea etc.
3. In the manufacture of synthetic petrol.
4. In the atomic hydrogen torch and oxy hydrogen torches for cutting and welding. Dihydrogen is dissociated with the help of an electric arc and the hydrogen atoms produced are allowed to recombine on the surface to be welded. High temperature of about 4000 k is generated.
5. In the fuel cell for generating electrical energy.

★Ortho and parahydrogens:-A molecule of dihydrogenabc



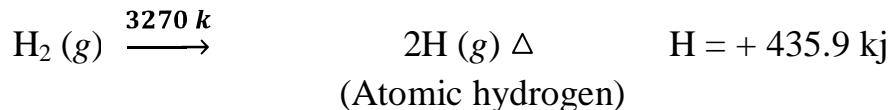
- They show different physical properties. For example :

 - (i) The thermal conductivity of para hydrogen is about 50 % greater than that of ortho hydrogen.
 - (ii) The melting point of para hydrogen is 0.15 k below that of hydrogen containing 75% ortho hydrogen.

- They show similar chemical properties.

★Atomic hydrogen:-

- Because of high H—H bond enthalpy, atomic hydrogen is produced only at high temp in an electric arc or under ultraviolet radiation.



- Highly reactive.
- Half life period is 0.3 sec and therefore, it immediately gets converted into the molecular form liberating a large amount of energy which is used for cutting and welding purposes.

★ **Nascent hydrogen:**-The hydrogen produced in contact with the substance to be reduced is known as ‘nascent hydrogen’. It is very reactive form of hydrogen better reducing agent than ordinary dihydrogen.

★ **Hydrides:**-Under certain conditions H₂ combines with almost all the elements ,except noble gases to form compounds called hydrides.

➤ There are three types of hydrides ,they are

- (i) Ionic or saline hydrides
- (ii) Covalent or molecular hydrides (iii) Metallic or non-stoichiometric hydrides

Ionic or saline hydrides:-

➤ These are the compounds of H₂ formed with most of the s-block elements which are highly electro positive.

(ii) Covalent or molecular hydrides:-These are the compounds of hydrogen formed with most of the p-block elements

[a]Electron deficient:- The hydrides which do not have sufficient number of electrons to form normal covalent bonds is called electron deficient hydride. For example, hydride of group 13 (BH₃, AlH₃, etc.).They are known as Lewis acids i.e., electron acceptors. To make up their deficiency they generally exist in polymeric forms such as B₂H₆, Al₂H₆, etc.

[b] Electron precise:-The hydrides which have sufficient number of electrons required for forming covalent bonds is called electron precise hydride. For example, hydrides of group 14 (CH₄, SiH₄, GeH₄, SnH₄, PbH₄ etc.) they have tetrahedral geometry.

[c] Electron rich hydrides:-The hydrides which have excess electrons as required to form normal covalent bonds is called electron rich hydride. For example, hydrides of group 15 to 17 (NH₃, PH₃, H₂O, H₂S, H₂Se, H₂Te, HF etc.)

(iii) Metallic or non-stoichiometric hydrides:-

➤ *These are formed by many d-block and f-block elements*

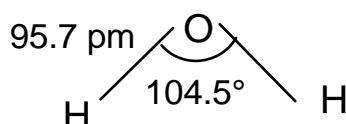
➤ *These hydrides conducts heat and electricity though not efficient.*

★ **Water:** -Water! It is the major part of all living organisms. water is also known as the river of life.

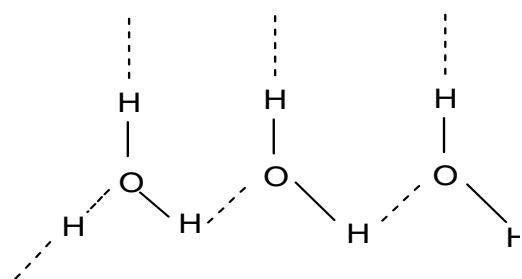
➤ Human body has about 65% and some plants have as much as 95% water.

❖ STRUCTURE OF WATER:-

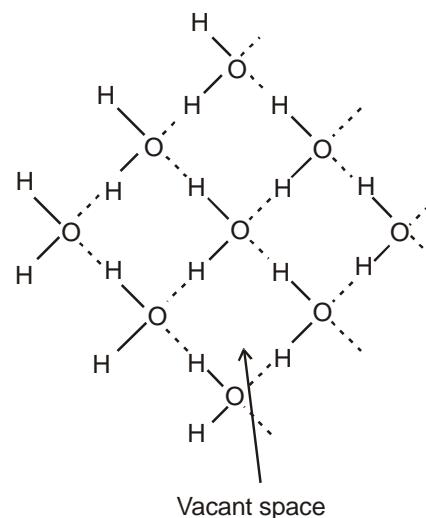
➤ In a gas phase water is bent molecule with a bond angle of 104.5° and O-H bond length of 95.7 pm It is highly polar molecule.



Solid state



- ❖ **Structure of ice**:-Ice has a highly ordered 3D hydrogen bonded structure. Each oxygen atom is surrounded tetrahedrally by four other four other oxygen atoms at a distance of 276 pm



★Chemical Properties of water:-

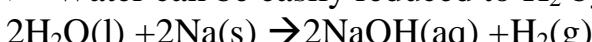
- [i] **AMPHOTERIC NATURE**:-It has the ability

.it acts as an acid with NH_3 and as a base with H_2S

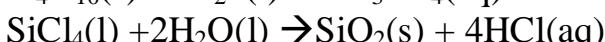
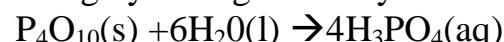


- [ii] **REDOX REACTIONS INVOLVING WATER**:-

➤ Water can be easily reduced to H_2 by highly electropositive metals



- [iii] **HYDROLYSIS REACTION**:-Due to high dielectric constant, it has a very strong hydrating tendency .it dissolves many ionic compounds



- [iv] **HYDRATES FORMATION**:-From the aqueous solutions many salts can be crystallized as hydrated salts. It of different types.

(1) Coordinated water e.g., $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} \ 3\text{Cl}^-$

(2) Interstitial water e.g., $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$

(3) hydrogen-bonded water e.g. $[\text{Cu}(\text{H}_2\text{O})_4]^{2+} \ 4\text{SO}_4^{2-} \cdot \text{H}_2\text{O}$ in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

★Hard & Soft Water:-

- The water which contains dissolved salts of bicarbonates, sulphates and chlorides of calcium and magnesium is called hard water. Hard water does not produce lather with soap solution.
- Soft water is free from bicarbonates, sulphates and chlorides of calcium and magnesium. It produces lather with soap solution easily. e.g., distilled water, rain water..

★Types of hardness:-The hardness of water is of two types

(i)Temporary hardness

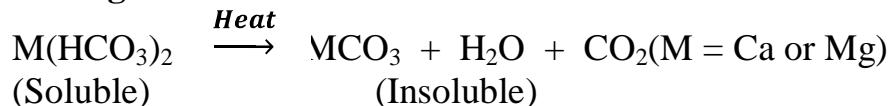
- Due to presence of soluble bicarbonates of calcium and magnesium.
- Can be removed by simple boiling.

(ii)Permanent hardness

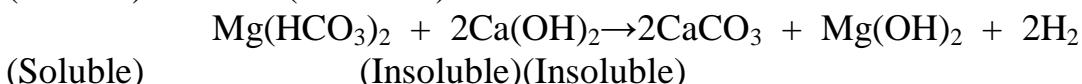
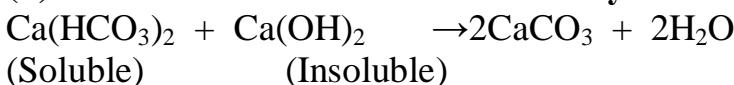
- Due to presence of chlorides and sulphates of calcium and magnesium.
 - Requires treatment of water to remove this type hardness.
 - ***Do you know?***
 - Temporary hardness is also called carbonate hardness &
 - Permanent hardness is also called non-carbonate hardness
 - ★ **Softening of water:-**The process of removal of Ca^{2+} and Mg^{2+} ions from water is called softening of water.

❖ Removal of temporary hardness:-

(i) By boiling :

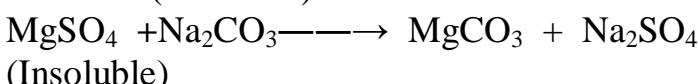
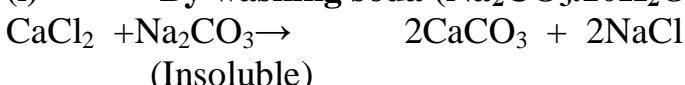


(ii) Clark's method or calcium hydroxide method

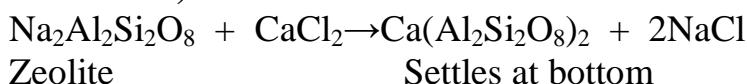


❖ Removal of permanent hardness:-

(i) By washing soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) treatment:



(ii) By using inorganic cation exchanger (permutit method or Zeolite method):

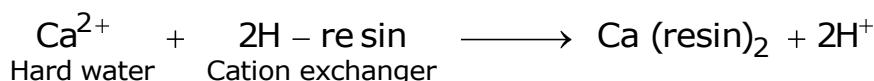


The zeolite can be regenerated by treatment with sodium chloride solution.

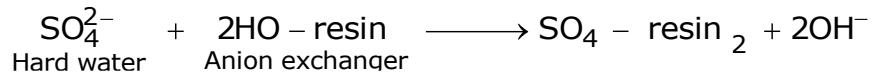


(iii) By organic ion exchanger or synthetic resins (ion exchange resins):-

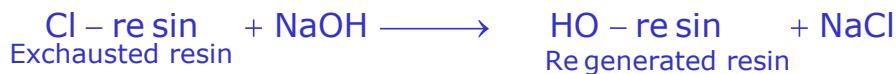
- Synthetic resins are the insoluble polymeric solids having giant hydrocarbon network containing reactive acidic or basic groups. These are superior to Zeolite because they can remove all types of cations as well as anions present in water. This resulting water is known as demineralised or deionised water.
 - These are two types:
 - (a) **Cation exchanger resins:** they have acidic groups such as COOH or SO₃H. They may be represented as resin—H⁺



- (b) **Anion exchanger resins:** they have basic groups such as $-OH^-$ or $-NH_2$. they may be represented as **resin—OH⁻** or **resin—NH₃⁺OH⁻**



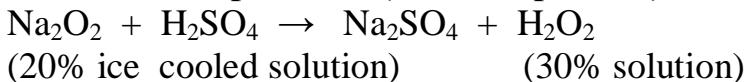
Regeneration of resins:



★ **Hydrogen peroxide [H₂O₂]:-** discovered by French chemist J.L. Thenard

❖ **Methods of preparation**

- 1) **From sodium peroxide (Merck's process):-**



2. **From Barium peroxide:-**

➤ Hydrogen peroxide was first prepared by J. L. Thenard in 1818 by acidifying barium peroxide and removal of excess water by evaporation under reduced pressure.



➤ Barium sulphate is filtered off leaving behind H₂O₂.

Store of Hydrogen peroxide:-

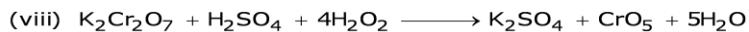
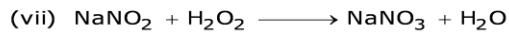
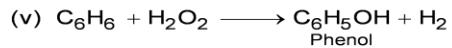
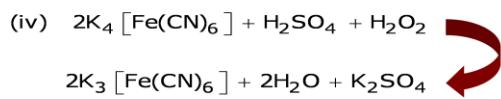
- It must be kept in wax lined coloured bottles because the rough glass surface causes its decomposition.
- A small amount of phosphoric acid , glycerol or acetanilide is generally added which retard the decomposition of H₂O₂. These are also called negative catalysts.

❖ **Physical properties of Hydrogen peroxide:-**

- In the pure state H₂O₂ is an almost colourless(very pale blue) liquid.
- H₂O₂ is miscible with water in all proportions and forms a hydrate H₂O₂.H₂O (mp 221K).
- A 30% solution of H₂O₂ is marketed as '100 volume' hydrogen peroxide. It means that one millilitre of 30% H₂O₂ solution will give 100 V of oxygen at STP. Commercially, it is marketed as 10 V, which means it contains 3% H₂O₂.

Chemical properties of Hydrogen peroxide:-

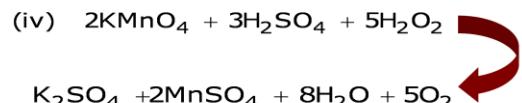
Oxidising properties



Reducing properties



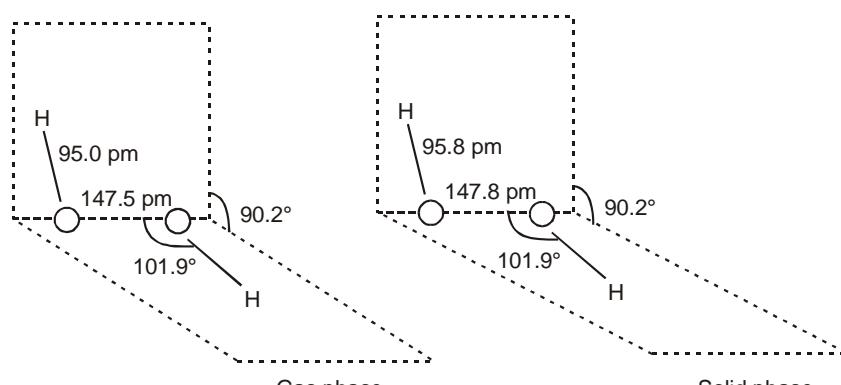
Reducing properties



❖ Uses of hydrogen peroxide

- 1) For bleaching silk, wool, hair and leather
- 2) As rocket fuel

❖ Structure of hydrogen peroxide



Structure of hydrogen peroxide

Hydrogen economy (Hydrogen as fuel)

- ☞ The electricity cannot be stored to run automobiles. It is not possible to store and transport nuclear energy. Hydrogen is an alternative source of energy and hence called as 'hydrogen economy'. Hydrogen has some advantages as fuel
- ☞ Available in abundance in combined form as water.
- ☞ On combustion produces H_2O . Hence pollution free.
- ☞ H_2-O_2 fuel cell give more power.
- ☞ Excellent reducing agent. Therefore can be used as substitute of carbon in reduction for processes in industry.

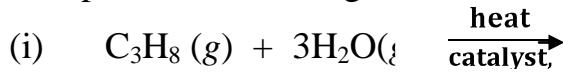
❖ Obstacles in hydrogen economy

☞ Transportation:

- ☞ Hydrogen gas is explosive and hence it is difficult to store and transport.
- ☞ Formation of hydrogen from H_2O :
- ☞ The cheaper production of the hydrogen is basic requirement of hydrogen economy which is not possible now.
- ☞ The main aim and advantage of hydrogen economy is to transmit energy in form of hydrogen.

One mark question:

1. What is meant by 10 volume hydrogen peroxide?
2. Why is dihydrogen gas not preferred in balloons?
3. Name the constituents of water gas.
4. Name one compound each in which hydrogen exists in (i) positive oxidation state, and (ii) Negative oxidation state.
5. What type of elements form interstitial hydrides?
6. How many hydrogen bonded water molecule(s) are present in $CuSO_4 \cdot 5H_2O$?
7. What happens when heavy water is added to calcium carbonate?
8. Concentrated sulphuric acid cannot be used for drying H_2 . Why?
9. Complete the following reactions?

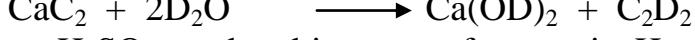


10. How heavy water is obtained from ordinary water?

Solutions:

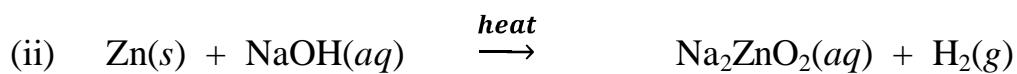
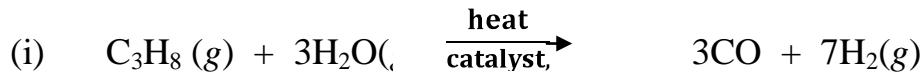
1. It means that 1 ml of H_2O_2 will give 10 ml of oxygen at N.T.P.
2. Dihydrogen gas is combustible in nature. Therefore, it may react with oxygen highly violently. Thus, it is not used in balloons.
3. Carbon monoxide and hydrogen.

4. (i) HCl (ii) NaH
5. Elements of d-and f-block.
6. In CuSO₄.5H₂O, there is one hydrogen bonded water molecule which is outside the coordination sphere. The other four molecules of water are coordinated.
7. Deutero acetylene is formed.



8. Conc. H₂SO₄ on absorbing water from moist H₂ produces so much heat that H₂ catches fire.

9.



10. Heavy water is obtained from ordinary water by repeated electrolysis in the presence of 3% NaOH.

Two mark question

1. Can we use concentrated sulphuric acid and pure zinc in the preparation of dihydrogen?
2. Write the chemical reactions to show the amphoteric nature of water.
3. Why is hydrogen peroxide stored in wax-lined plastic coloured bottles?
4. H₂O₂ acts as an oxidizing agent as well as reducing agent. Why?
5. What causes the temporary and permanent hardness of water?

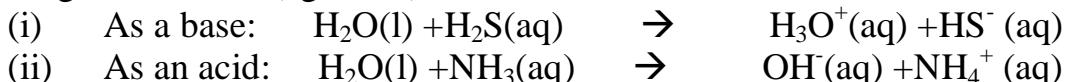
Solutions:

1. (a) Conc. H₂SO₄ cannot be used because it acts as oxidizing agent also and gets reduced to SO₂.



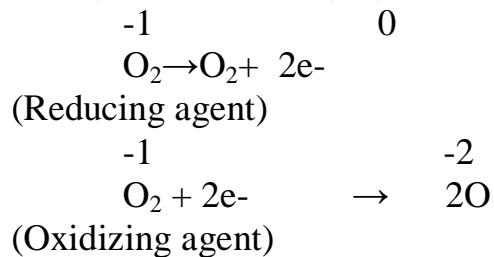
(b) Pure Zn is not used because it is non-porous and reaction will be slow. The impurities in Zn help in constitute of electrochemical couple and speed up reaction.

2. Water is amphoteric in nature and it behaves both as an acid as well as a base. With acids stronger than itself (eg., H₂S) it behaves as a base and with bases stronger than itself (eg. NH₃) it acts as an acid.



3. The decomposition of H₂O₂ occurs readily in the presence of rough surface (acting as catalyst). It is also decomposed by exposure of light. Therefore, wax-lined smooth surface and coloured bottles retard the decomposition of H₂O₂.

4. In H_2O_2 , oxygen has -1 oxidation state which lies between maximum (0 or +2 in OF_2) and minimum -2. Therefore, oxygen can be oxidized to O_2 (zero oxidation state) acting as reducing agent or can be reduced to H_2O or OH^- (-2 oxidation state) acting as an oxidizing agent.



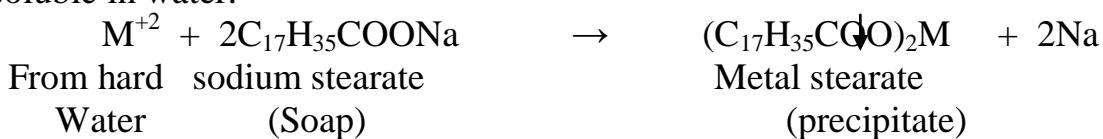
5. Temporary hardness is due to presence of soluble bicarbonates of calcium and magnesium. On the other hand, permanent hardness is due to presence of chlorides and sulphates of calcium and magnesium.

Three mark question:

1. Hard water is unsuitable for laundry, washing and dyeing. Explain.
2. What do you understand by (i) electron-deficient, (ii) electron-precise, and (iii) electron-rich compounds of hydrogen? Provide justification with suitable examples.
3. Compare the structures of H_2O and H_2O_2 .

Solutions:

1. Ans: - since we know that the soaps are the sodium salts of higher fatty acids like stearic acid ($\text{C}_{17}\text{H}_{35}\text{COOH}$), oleic acid ($\text{C}_{17}\text{H}_{33}\text{COOH}$) or palmitic acid ($\text{C}_{17}\text{H}_{31}\text{COOH}$). When soap is added to hard water, the anions of soap combine with Ca^{+2} and Mg^{+2} ions to form calcium and magnesium salt which are insoluble in water.



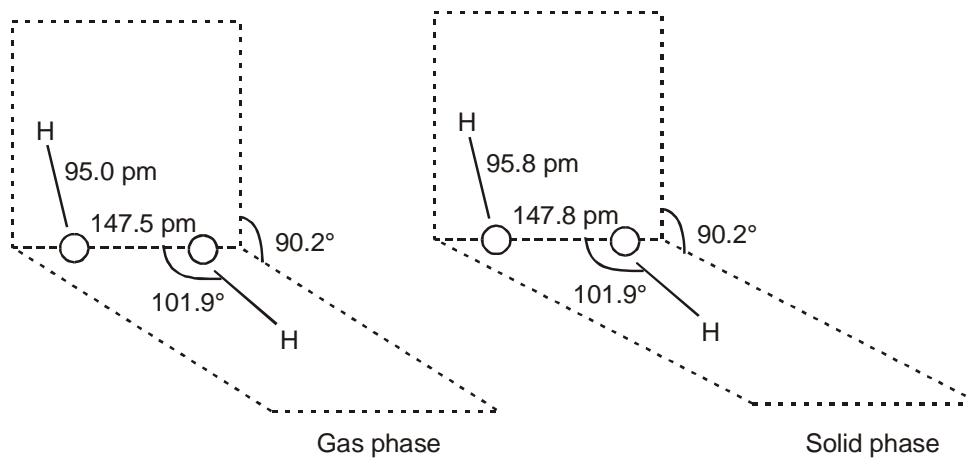
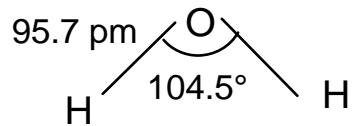
Therefore, no lather is produced until all the calcium and magnesium ions are precipitated. This also results into wastage of lot of soap. So hard water is unsuitable for laundry, washing and dyeing.

2. [a] **Electron deficient**:- The hydrides which do not have sufficient number of electrons to form normal covalent bonds are called electron deficient hydride. For example, hydride of group 13 (BH_3 , AlH_3 , etc.).
- [b] **Electron precise**:- The hydrides which have sufficient number of electrons required for forming covalent bonds are called electron precise hydride. For

example, hydrides of group 14 (CH_4 , SiH_4 , GeH_4 , SnH_4 , PbH_4 etc.) they have tetrahedral geometry.

[c] Electron rich hydrides:-The hydrides which have excess electrons as required to form normal covalent bonds is called electron rich hydride. For example, hydrides of group 15 to 17 (NH_3 , PH_3 , H_2O , H_2S , H_2Se , H_2Te , HF etc.)

3. In water, O atom is sp^3 hybridised and there are two O—H bonds and two sp^3 hybrid orbitals occupy lone pairs of ele
stronger lone pair-lone pair repulsions than bond
pair-bond pair repulsions, the H-O-H bond decreases from
109.5 to 104.5° . Therefore, water molecule is a bent or
angular molecule. H_2O_2 has non-planar structure. In this structure, two O—O
oxygen atoms are bonded to each other by a single covalent bond and each O
atom is further bonded to a hydrogen atom by a single covalent bond. The two
O—H bonds are in different planes in 111.50 in the gas phase.



Structure of hydrogen peroxide

Chapter 10

The s- Block Element

Important points

- Groups (1 & 2) belong to the s-block of the Periodic Table.
- Group 1 consists of : lithium, sodium, potassium, rubidium, caesium and francium and collectively known as the *alkali metals*.
- Group 2 include : beryllium, magnesium, calcium, strontium, barium and radium. Except Beryllium they are known as *alkaline*

❖ Physical properties-

- a) **Large atomic radii:** The atomic radii of alkali metals are the largest in their respective periods. These increase as we travel down the group.
- b) **Large ionic radii:** The ionic radii increase as we move down the group due to the addition of a new energy shell with each succeeding element.
- c) **Low ionization enthalpy:** The ionization enthalpies decrease as we move down the group. The ionization enthalpies of the alkali metals are the lowest due to loosely held s- electron.
- d) **Hydration enthalpy:** It decreases with the increase in ionic radii. The hydration enthalpy of Li ion is the maximum and the hydration enthalpy of Cs ion is the minimum.
- e) **Oxidation state:** The alkali metals exhibit oxidation state of +1 in their compounds and are strongly electropositive in character. The electropositive character increases from Li to Cs.
- f) **Metallic character:** The metallic character increases down the group.
- g) **Melting point and boiling point:** The m p and b p of alkali metals are very low and decrease with increase in atomic number.
- h) **Nature of bonds formed:** These metals form ionic bonds. The ionic character increases as we down the group.
- i) **Flame colouration:** All the alkali metals impart a characteristic colour to the flame.
- j) **Photoelectric effect:** Alkali metals (except Li) exhibits photoelectric effect.

❖ Chemical features of alkali metals:

- a) **Reducing character:** As the ionization enthalpies of the alkali metals decrease down the group their reducing character or reactivity in the gaseous state increases down the group. i.e., $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$.
- b) **Reaction with dihydrogen:** Alkali metals react with dry hydrogen at about 673 K to form crystalline hydrides which are ionic in nature and have high melting points.



- c) **Oxides and hydroxides:** Alkali metals when burnt in air form different compounds, for example the alkali metals on reaction with limited quantity of oxygen form normal oxides (M_2O) $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$

- d) **Reaction with halogens:** The members of the family combine with halogen to form corresponding halides which are ionic crystalline solids.
- Reactivity of alkali metals with particular halogen increases from Li to Cs.
- e) **Reaction with water:** Alkali metals react with water and other compounds containing acidic hydrogen atoms such as hydrogen halides, acetylene etc. to liberate hydrogen gas.
- f) **Solubility in liquid ammonia:** All alkali metals dissolve in liquid ammonia giving deep blue solutions which are conducting in nature.
- g) **Reaction with sulphur and phosphorus:** Alkali metals react with sulphur and phosphorus on heating to form sulphides and phosphides respectively.

❖ Diagonal relationship between Li and Al

Li resembles Mg mainly due to similarity in sizes of their atoms and ions. The main points of similarity are:

- i) Both are quite hard.
- ii) Both LiOH and Mg(OH)₂ are weak bases.
- iii) Carbonates of both on heating decompose to produce oxides and carbondioxide.
- iv) Both react with nitrogen to give ionic nitrides.
- v) Nitrates of both decompose on heating to give oxides.
- vi) Both Li and Mg do not form solid bicarbonates.
- vii) Because of covalent character LiCl and MgCl₂ are soluble in ethanol.
- viii) The hydroxides, bicarbonates and fluorides of both Li and Mg are sparingly soluble in water.

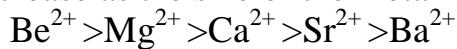
❖ Biological importance of Na and K

- i) Sodium ions participate in the transmission of nerve signals.
- ii) Sodium ions also regulate flow of water across the cell membranes and in transport of sugars and amino acids into the cells.
- iii) Potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in oxidation of glucose to produce ATP.
- iv) Potassium ions in combination with sodium ions are responsible for transmission of nerve signals.
- v) The functional features of nerve cells depend upon the sodium potassium ion gradient that is established in the cell.

❖ Group 2 elements: Alkaline earth metals

- (a) **Atomic radii :** The atomic radii of alkaline earth metals are fairly large though smaller than the corresponding alkali metals and they increase down the group. This is because on moving down the group, atomic radii increase primarily due to the addition of an extra shell of electrons in each succeeding element.
- (b) **Ionic radii:** the atoms of these elements form divalent ions which show the same trend of increase in their size down the group.
- (c) **Ionization enthalpy:** The alkaline earth metals have fairly low Ionizations enthalpies though greater than those of the corresponding elements of group 1 and this value decreases down the group.

(d) Hydration enthalpy: the Hydration enthalpies of alkaline earth metal ion decrease as the size of the metal ion increases down the Group



(e) Oxidation State: All the members of the family exhibit +2 oxidation state in their compounded and the form divalent cations (M^{2+})

(f) Electro negativity : The electro negativity values of alkaline earth metals are quite close to those of alkali metals, though slightly more.

(g) Metallic Character : Alkaline earth metals have stronger metallic bonds as compared to the alkali metals present in the same period.

(h) Melting and boiling point : The melting and Boiling points of these metals are higher than those of alkali metals present in the same period.

(i) Colouration to the flame : With the exception of beryllium and magnesium, the rest of the elements impart characters in colour to the same flame. For example,

| | | | | | |
|----|----|-----------|---------|--------------|---------|
| Be | Mg | Ca | Sr | Ba | Ra |
| - | - | Brick Red | Crimson | Grassy Green | Crimson |

J) Complex formation: Generally the members do not form complexes. However, smaller ions (Be & Mg Ions) form complexes with the electron donor species

k) Formation of organo-metallic compounds: Both beryllium and magnesium form a number of organo-metallic compounds containing M-C bond with certain organic compounds. For example, magnesium reacts with alkyl halide in the presence of dry ether to give Grignard reagent.

l) Reducing character: Alkaline earth metals are weak reducing agent than the corresponding alkali metals which have lower ionization enthalpies and comparatively bigger atomic sizes.

m) Reaction with oxygen: With the exception of Ba and Ra which form peroxides (MO_2) rest of the metals form normal oxides (MO) on heating with excess of oxygen.

n) Reaction with halogens: The members of the family combine directly with halogen at appropriate temperature to form corresponding halides.

o) Reaction with water: The members of this group are less reactive towards water as compared to the corresponding alkali metals because these are less electropositive in nature.

p) Reaction with hydrogen: The members except Be combine with hydrogen directly upon heating to form metal hydrides.

Uses of some important compounds:-

(i) Caustic soda:

It is used: in soap, paper, textile, petroleum industry

ii) Sodium carbonate

It is used:

- in glass and soap industry
- in paper making and textile manufacturing
- in paint and dye stuffs
- in metal refining

- e) in production of sodium compounds such as borax, caustic soda, sodium phosphate etc.

iii) Quick lime:

It is used:

- a. in the preparation of cement, glass and calcium carbide.
- b. In the purification of sugar
- c. In softening of hard water d. As a flux in the extraction of metal

iv) Lime stone: It is used

- a) as building material
- b) in the manufacture of quick lime
- c) in Solvay process to prepare Na_2CO_3 as it is a source of CO_2
- d) in metallurgy for the extraction of iron
- e) in toothpaste and certain cosmetics

v) Cement: It is an important building material. It is used in concrete and reinforced concrete, in plastering and in the construction of bridges, dams and buildings.

vi) Plaster of paris: It is used

- a) in making moulds for pottery and ceramics etc.
- b) in surgical bandages for setting broken bones of the body
- c) for making statues, models, decorative materials and black board chalk.

❖ Biological importance of Ca and Mg

- i) Magnesium ions are concentrated in animal cells and Calcium ions are concentrated in body fluids, outside the cell.
- ii) All enzymes that utilize ATP in phosphate transfer require magnesium ion as cofactor.
- iii) In green plants magnesium is present in chlorophyll.
- iv) Calcium and magnesium ions are also essential for the transmission of impulses along nerve fibres.
- v) Calcium ions are important in blood clotting and are required to trigger the contraction of muscles.
- vi) Calcium ions also regulate the beating of the heart.

One mark questions:

1. Why are halides of beryllium polymeric?

Ans:- the halides of Be are electron deficient as their octets are incomplete. Therefore, to complete their octets, the halides polymerize.

2. Name the groups which constitute s-block elements.

Ans:- group-1 and 2

3. Arrange the alkaline earth metal carbonates in the decreasing order of thermal stability.

Ans:- $\text{BaCO}_3 > \text{SrCO}_3 > \text{CaCO}_3 > \text{MgCO}_3 > \text{BeCO}_3$

4. Write the general electronic configuration of s-block elements.

Ans:- [Noble gas] ns^{1-2}

5. What is the chemical formula of Plaster of Paris?

Ans:- $\text{CuSO}_4 \cdot 1/2\text{H}_2\text{O}$

6. Name the compound which can be obtained by Solvay's process.

Ans:- Sodium carbonate

7. How does the basic character of hydroxides of alkali metals vary down the group?

Ans:- Increases down the group

8. Which out of $MgSO_4$ or $BaSO_4$ is more soluble in water?

Ans:- $MgSO_4$

9. Name radioactive elements of group 1 and 2.

Ans:- Francium and Radium.

10. Which elements of alkaline earth metals family do not give characteristic flame colouration?

Ans:- Be and Mg

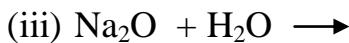
Two marks questions

1. Among the alkali metals which has

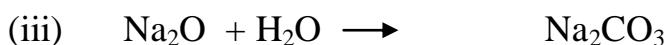
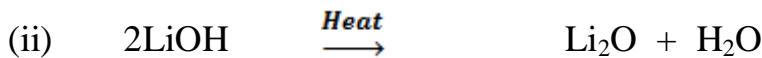
- (i) Highest melting point
- (ii) Most electropositive character
- (iii) Lowest size of ion
- (iv) Strongest reducing character.

Ans:- (i) Li (ii) Cs (iii) Li (iv) Li

2. Complete the following reactions:



Ans:-



3. Name the chief factors responsible for anomalous behaviour of lithium.

Ans:- the anomalous behaviour of lithium is because of its:

- (i) Small size of atom and ion,
- (ii) High ionization enthalpy, and
- (iii) Absence of d-orbitals in its Valence shell.

4. Which out of Li and Na has greater value for the following properties:

- (i) Hydration enthalpy
- (ii) Stability of hydride
- (iii) Stability of carbonate
- (iv) Basic character of hydroxide

Ans:- (i) Li (ii) Li (iii) Na (iv) Na

5. Why are alkali metals not found in nature?

Ans. Alkali metals are highly reactive in nature due to low ionization enthalpy and strong electropositive character. They do not occur in free state and are always combined with other elements. As a result alkali metals are not generally found in nature.

6. Why are lithium salts commonly hydrated and those of the other alkali ions usually anhydrous?

Ans. In the lithium salt, the Li^+ ion due to very small size gets readily hydrated on coming in contact with moisture (water). Therefore, lithium salts are commonly hydrated. But the other alkali metal ions are comparatively big in size. They have therefore, lesser tendency to get hydrated. These salts are usually anhydrous.

7. Beryllium and magnesium do not give colour to flame whereas other alkaline earth metals do so why?

Ans: Beryllium and magnesium atoms in comparison to other alkaline earth metals are comparatively smaller and their ionisation enthalpies are very high. Hence, the energy of the flame is not sufficient to excite their electrons to higher energy levels. These elements, therefore, do not give any colour in Bunsen flame.

7. Why are alkali metals soft and have low melting points?

Ans: Alkali metals have only one valence electron per metal atom. As a result, the binding energy of alkali metal ions in the close-packed metal lattices are weak. Therefore, these are soft and have low melting point.

8. Which out of the following and why can be used to store an alkali metal?

H_2O , $\text{C}_2\text{H}_5\text{OH}$ and Benzene

Ans:- Benzene can be used to store an alkali metal because other substance react with alkali metal as:



9. Why are alkali metals not found free in nature?

Ans:- alkali metals are highly reactive and therefore, are not found free in nature, they are present in the combined state in the form of halides, oxides, silicates, nitrates, etc.

Three marks questions

1. When an alkali metal dissolves in liquid ammonia the solution can acquire different colours. Explain the reasons for this type of colour change.

Ans. The dissolution of the metal in liquid ammonia is accompanied by their formation of ammoniated electrons that give rise to dark colour. This is because ammoniated electrons absorb energy corresponding to the red region of the visible light. However, if the concentration increases above 3M, the colour changes to copper-bronze and the solution acquires metallic luster due to the formation of metal ion clusters.



2. In what ways lithium shows similarities to magnesium in its chemical behaviour?

Ans. Li resembles Mg mainly due to similarity in sizes of their atoms and ions. The main points of similarity are:

Both are quite hard.

1 Both LiOH and Mg(OH)₂ are weak bases.

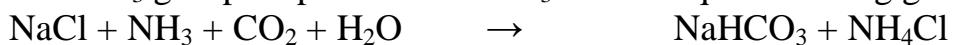
2 Carbonates of both on heating decompose to produce oxides and carbondioxide.

3 Both react with nitrogen to give ionic nitrides.

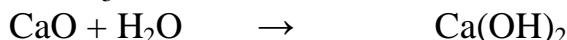
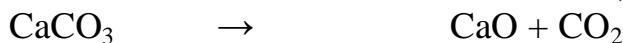
3. Discuss the various reactions that occur in the Solvay process.

Ans. In Solvay ammonia process.

When carbon dioxide is passed through a concentrated solution of brine saturated with NH₃, NaHCO₃ gets precipitated. NaHCO₃ on subsequent heating gives Na₂CO₃.



CO₂ needed for the reaction is prepared by heating calcium carbonate and the quick lime, CaO is dissolved in water to form slaked lime, Ca(OH)₂



NH₃ needed for the purpose is prepared by heating NH₄Cl and Ca(OH)₂



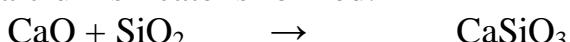
4. What happen when (i) magnesium is burnt in air (ii) quick lime is heated with silica (iii) chlorine reacts with slaked lime (iv) calcium nitrate is heated?

Ans. (i) A mixture of magnesium oxide and magnesium nitride is formed

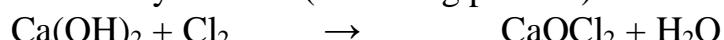


In air

(ii) Calcium silicate is formed.



(iii) Calcium oxychloride (bleaching powder) is formed



(iv) Nitrogen dioxide is evolved.



5. Describe the importance of the following (i) limestone (ii) cement (iii) plaster of paris.

Ans. i) Lime stone: It is used

- f) as building material
- g) in the manufacture of quick lime
- h) in Solvay process to prepare Na₂CO₃ as it is a source of CO₂
- i) in metallurgy for the extraction of iron
- j) in toothpaste and certain cosmetics

ii) Cement: It is an important building material. It is used in concrete and reinforced concrete, in plastering and in the construction of bridges, dams and buildings.

iii) Plaster of paris: It is used

- d) in making moulds for pottery and ceramics etc.
- e) in surgical bandages for setting broken bones of the body
- f) for making statues, models, decorative materials and black board chalk.

6. What happens when:

- a) Sodium metal is dropped in water?
- b) Sodium metal is heated in free supply of air?
- c) Sodium peroxide dissolves in water?

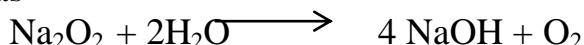
Ans. a) Sodium metal catches fire and hydrogen gas is evolved



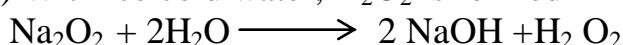
b) Sodium peroxide is formed



c) (i) Sodium peroxide reacts with water at ordinary temperature to liberate oxygen gas



ii) With ice cold water, H_2O_2 is formed



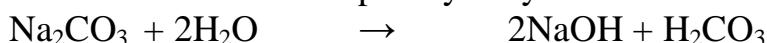
7. State as to why

a) a solution of Na_2CO_3 is alkaline?

b) alkali metals are prepared by electrolysis of their fused chlorides?

c) sodium is found to be more useful than potassium?

Ans. (a) Sodium carbonate being a salt of strong base (NaOH) and weak acid (H_2CO_3) forms alkaline solution upon hydrolysis



(b) Since the discharge potential of alkali metals is much higher than that of hydrogen, therefore, when the aqueous solution of any alkali metal chloride is subjected to electrolysis, H_2 instead of the alkali metal is produced at the cathode. Therefore, to prepare alkali metals, electrolysis of their fused chlorides is carried out.

(c) Sodium is relatively more abundant than potassium. At the same time, it is also less reactive and its reactions with other substances can be better controlled.

8. Why are potassium and cesium, rather than lithium used in photoelectric cells?

Ans. The ionization enthalpy of lithium is quite high. The photons of light are not in a position to eject electrons from the surface of lithium metal. Therefore photoelectric effect is not noticed. However, both potassium and cesium have comparatively low ionization enthalpies. This means that the electrons can quite easily be ejected from the surface of these metals when photons of certain minimum frequency (threshold frequency) strike against their surface

9. Why is Li_2CO_3 decomposed at a lower temperature whereas Na_2CO_3 at higher temperature?

Ans. Li^+ ion is very small in size. It is stabilized more by smaller anions such as oxide ion rather than large anions such as carbonate. Therefore Li_2CO_3 decomposes into Li_2O on mild heating. On the other hand, Na^+ ion is larger in size. It is stabilized

more by carbonate ion than oxide ion. Hence, Na_2CO_3 does not undergo thermal decomposition easily.

10. Explain why can alkali and alkaline earth metals not be obtained by chemical reduction methods?

Ans. The metals belonging to both these families are very strong reducing agents. It is therefore not possible to reduce their oxides by reacting with common reducing agents like carbon (coke), zinc etc. These are normally isolated by carrying out the electrolysis of the salts of these metals in the molten state.

Five marks questions:

1. Compare the solubility and thermal stability of the following compounds of the alkali metals with those of the alkaline earth metals.(a) Nitrates (b) Carbonates (c) Sulphates.

Ans. Solubility:

In case of alkali metals: Nitrates, carbonates and sulphates of alkali metals are soluble in water. In alkali metals lattice energies decrease more rapidly than the hydration energies, therefore their solubility increases down the group.

In case of alkaline earth metals: Nitrates of all alkaline earth metals are soluble in water but their solubility decreases down the group because their hydration energies decrease more rapidly than their lattice energies.

Since the size of CO_3^{2-} and SO_4^{2-} anions is much larger than the cations, therefore lattice energies remain almost constant with in a particular group. Since, the hydration energies decrease as we move down the group, therefore the solubility of alkaline earth metal carbonates and sulphates decrease down the group. However, the hydration energy of Be^{2+} and Mg^{2+} ions overcome the lattice energy factor and therefore BeSO_4 and MgSO_4 are readily soluble in water while the solubility of other sulphates decreases down the group from CaSO_4 to BaSO_4 .

Thermal Stability:

- a) Nitrates: Nitrates of both alkali and alkaline earth metals decompose on heating.

All alkaline earth metal nitrates decompose to form metal oxide, NO_2 and O_2 .

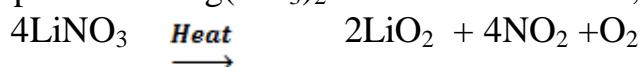


M= Be, Mg, Ca, Sr, or Ba

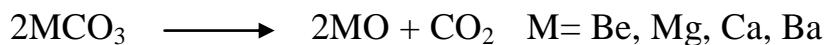
The nitrates of Na, K, Rb and Cs decompose to form metal nitrites and O_2 .



However, due to diagonal relationship between Li and Mg, lithium nitrate decomposes like $\text{Mg}(\text{NO}_3)_2$ to form metal oxide, NO_2 and O_2 .

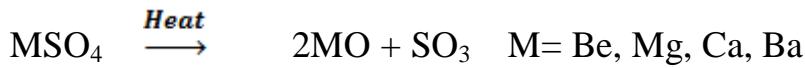


- b) Carbonates: Carbonates of alkaline earth metals decompose on heating to form metal oxide and carbon di oxide.



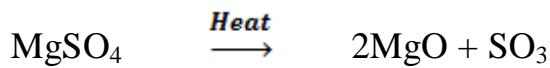
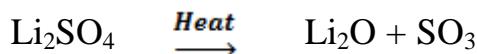
Further as the electropositive character of the metal increases down the group the stability of these metal carbonates increases or the temperature of their decomposition increases.

c) Sulphates: Sulphates of alkaline earth metals decompose on heating to form metal oxide and SO_3 .



The temperature of decomposition of these sulphates increases as the electropositive character of the metal or the basicity of the metal hydroxide increases down the group.

Among the alkali metals due to diagonal relationship, Li_2SO_4 decomposes like MgSO_4 to form the corresponding metal oxide and SO_3 .



Other alkali metals are stable to heat and do not decompose easily.

2. Compare the alkali metals and alkaline earth metals with respect to (i) ionization enthalpy (ii) basicity of oxides and (iii) solubility of hydroxides..

Ans.

- (i) Ionization enthalpy (I E): I E of alkaline earth metals are higher than those of alkali metals of group 1. This is because the atoms of alkaline earth metals have smaller size (due to higher nuclear charge) as compared to the alkali metals.
- (ii) Basicity of oxides: The oxides of alkali and alkaline earth metals dissolve in water to form their respective hydroxides. These hydroxides are strong bases. The hydroxides of alkaline earth metals are less basic than of alkali metals of the corresponding periods. This is due to their (i) high ionization enthalpy (ii) small ionic size and (iii) dipositive charge on the ions.

As a result M-O bond in these hydroxides is relatively stronger than that of corresponding alkali metals and therefore does not break.

- (iii) Solubility of hydroxides: Because of smaller size and higher ionic charge, the lattice enthalpies of alkaline earth metals are much higher than those of alkali metals and hence the solubility of alkali metal hydroxides is much higher than that of alkaline earth metals. However the solubility of the hydroxides of both alkali and alkaline earth metals increase down the group due to large decrease in their lattice enthalpies as compared to their hydration enthalpies.

3. Explain the significance of sodium, potassium, magnesium and calcium in biological fluids.

Ans. Significance of sodium and potassium:

- (i) Sodium ions participate in the transmission of nerve signals.
- (ii) Sodium ions also regulate flow of water across the cell membranes and in transport of sugars and amino acids into the cells.
- (iii) Potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in oxidation of glucose to produce ATP.

- (iv) Potassium ions in combination with sodium ions are responsible for transmission of nerve signals.
- (v) The functional features of nerve cells depend upon the sodium potassium ion gradient that is established in the cell.

Significance of Magnesium and Calcium:

1. Magnesium ions are concentrated in animal cells and Calcium ions are concentrated in body fluids, outside the cell.
2. All enzymes that utilize ATP in phosphate transfer require magnesium ion as cofactor.
3. In green plants magnesium is present in chlorophyll.
4. Calcium and magnesium ions are also essential for the transmission of impulses along nerve fibres.
5. Calcium ions are important in blood clotting and are required to trigger the contraction of muscles.
6. Calcium ions also regulate the beating of the heart.

HOTS QUESTIONS

1. Potassium carbonate cannot be prepared by Solvay process. Why?

Ans. This is due to the reason that potassium bicarbonate (KHCO_3) formed as an intermediate (when CO_2 gas is passed through ammoniated solution of potassium chloride) is highly soluble in water and cannot be separated by filtration.

2. The hydroxides and carbonates of sodium and potassium are easily soluble in water while the corresponding salts of magnesium and calcium are sparingly soluble in water. Explain.

Ans. All the compounds are crystalline solids and their solubility in water is guided by both lattice enthalpy and hydration enthalpy. In case of sodium and potassium compounds, the magnitude of lattice enthalpy is quite small as compared to hydration enthalpy since the cationic sizes are large. Therefore, the compounds of sodium and potassium that are mentioned, readily dissolve in water. However, in case of corresponding magnesium and calcium compounds, the cations have smaller sizes and more magnitude of positive charge. This means that their lattice enthalpies are more as compared to the compounds of sodium and potassium. Therefore, the hydroxides and carbonates of these metals are only sparingly soluble in water.

3. Why is LiF almost insoluble in water whereas LiCl soluble not only in water but also in acetone?

Ans. The low solubility of LiF in water is due to its very high lattice enthalpy (F^- ion is very small in size). On the other hand, in lithium chloride (LiCl) the lattice enthalpy is comparatively very small. This means that the magnitude of hydration enthalpy is quite large. Therefore lithium chloride dissolves in water. It is also soluble in acetone due to dipolar attraction. (Acetone is polar in nature)

CHAPTER 11

The p-block elements

Elements in which the last electron enters in the any one of the three p- orbital of their outermost shells – p-block elements

- Gen. electronic configuration of outer shell is $ns^2 np^{1-6}$

The inner core of e-config. may differ which greatly influences their physical & to some extent chemical properties.

- The block of elements in the periodic table consisting of the main groups :
- Group 13 (B to Tl)
- Group 14 (C to Pb)
- Group 15 (N to Bi)
- Group 16 (O to Po)
- Group 17 (F to At)
- Group 18 (He to Rn)

(1) Members at the top and on the right of the *p*-block are nonmetals (C, N, P, O, F, S, Cl, Br, I, At).

(2) Those on the left and at the bottom are metals (Al, Ga, In, Tl, Sn, Pb, Sb, Bi, Po).

(3) Between the two, from the top left to bottom right, lie an ill-defined group of metalloid elements (B, Si, Ge, As, Te)

GROUP 13 : The boron group

- Outer Electronic Configuration:- $ns^2 np^1$
- group members: boron (B), aluminum (Al), gallium (Ga), indium (In)& thallium (Tl). All, except boron, are metals.
- Boron show diagonal relationship with Silicon; both are semiconductors metalloids & forms covalent compounds.
- Boron compounds are electron deficient, they are lack of an octet of electrons about the B atom .
- diborane B_2H_6 , is simplest boron hydride

- Structure: three-center two-electron: the H atoms are simultaneously bonded to two B atoms the B-H bridging bond lengths are greater than B-H terminal.
- - Boron oxide is acidic (it reacts readily with water to form boric acid)
- aluminium compounds:aluminium oxide is amphoteric
- aluminum halides, e.g., AlCl_3 is dimer, an important catalyst in organic chemistry have an incomplete octet, acts as Lewis acid by accepting lone pairs from Lewis bases, forming adduct
- aluminum hydride, e.g., LiAlH_4 , a reducing agent
- Atomic Properties - Electronic Configurations

| Element | Symbol | Atomic No. | Electronic Configuration | Abundance in Earth's Crest (in ppm) |
|-----------|--------|------------|---|-------------------------------------|
| Boron | B | 5 | [He]2s ² 2p ¹ | 8 |
| Aluminium | Al | 13 | [Ne]3s ² 3p ¹ | 81,300 |
| Galium | Ga | 31 | [Ar]3d ¹⁰ 4s ² 4p ¹ | 15 |
| Indium | In | 49 | [Kr] 4d ¹⁰ 5s ² 5p ¹ | 1 |
| Thallium | Tl | 81 | [Xe] 5d ¹⁰ 6s ² 6p ¹ | 0.3 |

. Atomic and ionic radii

- The atomic and ionic radii of group 13 elements are compared to corresponding elements of group 2. From left to right in the period, the magnitude of nuclear charge increases but the electrons are added to, the same shell. These electrons do not screen each other, therefore, the electrons experience greater nuclear charge.
- In other words, effective nuclear charge increases and thus, size decreases. Therefore, the elements of this group have smaller size than the corresponding elements of second group.
- On moving down the group both atomic and ionic radii are expected to increase due to the addition of new shells. However, the observed atomic radius of Al (143 pm) is slightly more than that of Ga (135 pm).

Ionization energies

The first ionization energies of group 13 elements are less than the corresponding members of the alkaline earths.

The sharp decrease in I.E. from B to Al is due to increase in size. In case of Ga, there are ten d-electrons in its inner electronic configuration.

The very high value of 3rd I. E. of thallium indicates that +3 O.N. state is not stable, rather +1 is more stable for thallium .

Electropositive (or metallic) character

the elements of group 13 are less electropositive as compared to elements of group 2. On moving down the group the electropositive (metallic) character increases because ionization energy decreases. For e.g., Boron is a non-metal while the other elements are typical metals.

Oxidation states

The common oxidation states of group 13 elements are +3 and + 1 .The stability of the + 1 oxidation state increases in the sequence Al <Ga< In <Tl, Due to Inert pair effect.

| Element | B | Al | Ga | In | Tl |
|-----------------|----|----|--------|--------|--------|
| Oxidation state | +3 | +3 | +3, +1 | +3, +1 | +3, +1 |

Chemical reactivity of Gr.13 Elements

All elements in their compounds exhibit the oxidation state of + 3 and +1.

Hydrides

- None of the group 13 elements reacts directly with hydrogen. However, a no. of hydrides of these elements have been prepared by indirect methods. The boron hydrides are called boranes& classified in two series: (a) B_nH_{n+4} called nidoboranes (b) B_nH_{n+6} called arachnoboranes

- INUDUSTRIAL PREPERATION :-



- Laboratory method:

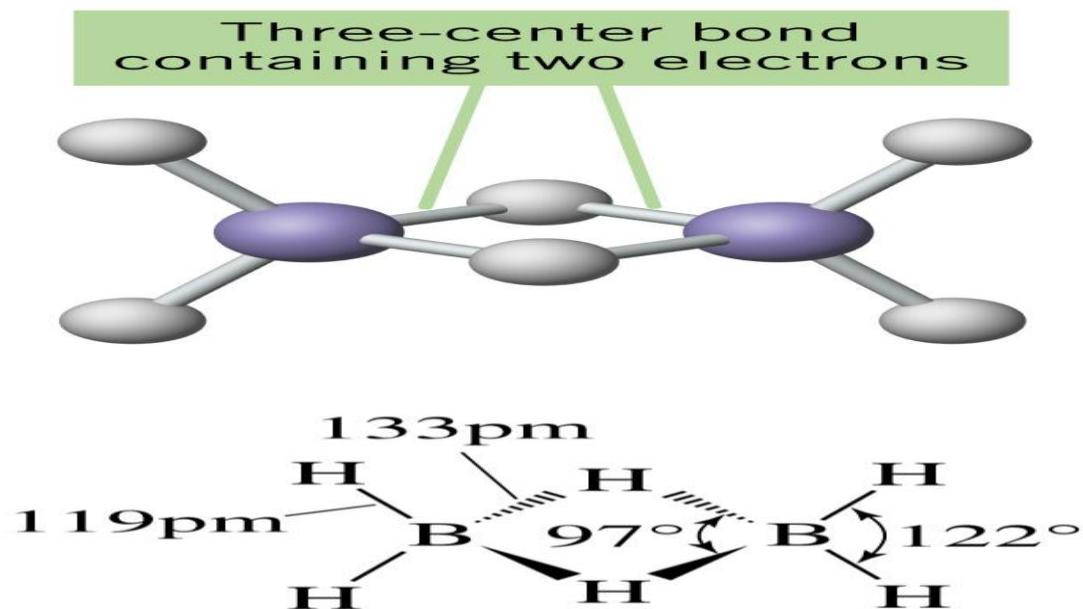
- (i) By the reaction of iodine with sodium borohydride in a high boiling solvent.



- (ii) By reduction of BCl_3 with $LiAlH_4$



Structure of Diborane, B_2H_6



Some important characteristics of boranes:

- Lower boranes are colourless gases while higher boranes are volatile liquids or solids.
- They undergo spontaneous combustion in air due to strong affinity of boron for oxygen.

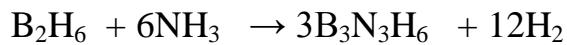


- Boranes react with alkali metal hydrides in diethyl ether to form borohydride complexes.



Metal borohydride

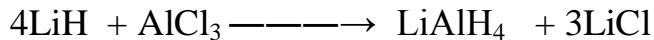
- (iv) Diborane reacts with ammonia to give borazine at 450 K.



- Borazine has a cyclic structure similar to benzene and thus is called inorganic benzene
- The other elements of this group form only a few stable hydrides. The thermal stability decreases as we move down the group.

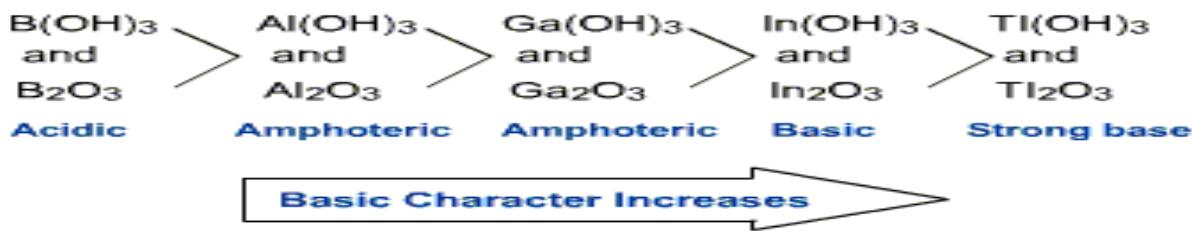
- AlH_3 is a colourless solid polymerized via Al - H - Al bridging units. These hydrides are weak Lewis acids and readily form adducts with strong Lewis base (B:) to give compounds of the type MH_3 ($\text{M} = \text{Al}$ or Ga). They also form complex-tetrahydrido anions, $[\text{MH}_4]^-$. The most important tetrahydrido compound is $\text{Li}[\text{AlH}_4]$

ether

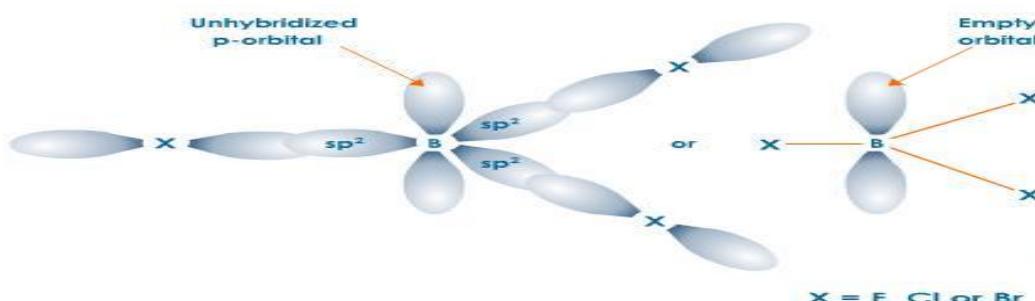


OXIDES & HYDROXIDES

- M_2O_3 & M(OH)_3



HALIDES: Structure of boron trihalides



Dimeric structure of aluminium chloride

- Boron halides do not form dimers because the size of boron is so small that it is unable to coordinate four large-sized halide ions.

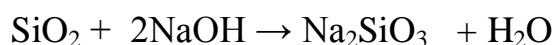
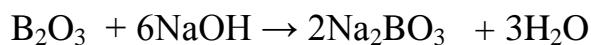


- Anomalous properties of boron

1. Boron is a non-metal & bad conductor of electricity whereas aluminium is a metal & good conductor. B is hard but Al is a soft metal.
2. Boron exists in two forms-crystalline and amorphous. But Al does not exist in different forms.

3. The melting and boiling point of boron are much higher than that of Al .
4. Boron forms only covalent compounds whereas Al forms even some ionic compounds.
5. The hydroxides and oxides of boron are acidic in nature whereas those of aluminium are amphoteric.
6. The trihalides of boron exist as monomers. On the other hand, aluminium halides exist as dimers .
7. The hydrides of boron are quite stable while those of aluminium are unstable

- Boron and silicon exhibit the typical properties of non-metals. These do not form cations. Both exist in amorphous as well as crystalline forms.
- Boron oxide (B_2O_3) and silica (SiO_2) both are acidic and dissolve in alkali solutions to form borates and silicates respectively.



- The chlorides of both B and Si get hydrolyzed by water to boric acid and silicic acid respectively.



- The hydrides of Boron and Silicon are quite stable. Numerous volatile hydrides are also known which catch fire on exposure to air and are easily hydrolyzed.
- Both elements are semiconductors.

Behavior in Aqueous Solutions

1 Al, Ga, In and Tl exhibit a well-defined aqueous chemistry in their tripositive states. Species like $[M(OH)4]^-$, $[M(H_2O)_2(OH)4]^-$, $[M(OH)_6]^{3+}$ for M = Al, Ga, In, exist in aqueous solution.

2. Al, Ga, In and Tl ions exist as octahedral aqua ions, $[M(OH)_6]^{3+}$ in aqueous solution and many salts like halides, sulphates, nitrates and perchlorates exist as hydrates.

3. Aluminiumsulphate forms double salts - called alum, having the general formula



USES OF BORON & ALUMINIUM

- Aluminium is used extensively in industry and everyday life. It forms many useful alloys with Cu, Mn, Mg, Si and Zn. Hence, aluminium and its alloys find use in packaging, utensil making, construction, aerospace and other transportation industries. It is used as a conductor for transmission of electricity. Aluminium is also used in the alumino-thermite process for production of chromium and manganese from their ores.

Group 14 Elements:-The Carbon Family

Group 14 includes carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb).

General electronic configuration of carbon family is ns^2np^2 .

Covalent radius:-Covalent radius expected to increase from C to Si,

From Si to Pb small increase is found.

Ionization Enthalpy:-The first ionization enthalpies of group 14 elements are higher than those of the corresponding group 13 elements.

Electronegativity:-Group 14 elements are smaller in size as compared to group 13 elements that's why this group elements are slightly more electronegative than group 13

Chemical properties:-

Carbon and silicon mostly show +4 oxidation state. Germanium forms stable compounds in +4 state and only few compounds in +2 state.

Tin forms compounds in both oxidation states. Lead compounds in +2 state are stable and in +4 state are strong oxidizing agents.

Exception:- Pb_4 and SnF_4 are ionic in nature.

Except CCl_4 other tetrachlorides are easily hydrolysed by water.

Since carbon does not have d-orbitals and hence cannot expand its coordination number beyond 4



Silicic acid

Allotropes of Carbon:-The three types of allotropes are –

1-Diamond

2-Graphite

3-Fullerene

Diamond:-In diamond each carbon atom undergoes SP^3 hybridisation.

Each carbon is tetrahedrally linked to four other carbon atoms.

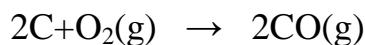
Graphite:-In graphite, carbon is SP^2 -hybridized graphite has a two-dimensional sheet like structure consisting of a number of hexagonal rings fused together.

Graphite conducts electricity along the sheet. It is very soft and Slippery

Fullerene was discovered collectively by three scientists namely R.E Smalley, R.F Curl and H.W Kroto

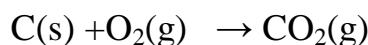
SOME Important Compounds Of Carbon and Silicon

Carbon monoxide:-It is prepared by direct oxidation of C in limited supply of oxygen.



Commercially it is prepared by the passage of steam over hot coke

Carbon Dioxide:-It is prepared by complete combustion of carbon and carbon fuels in excess of air.



Laboratory method:-

In laboratory it is prepared by the treatment of dilHCl on $CaCO_3$



Silicon dioxide:-Silicon dioxide is a COVALENT THREE DIMENSIONAL NETWORK SOLID.

Each silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms.

Silicones:-Silicones are the synthetic organo-silicon polymers having general formulae $(R_2SiO)_n$ in which R = alkyl (methyl, ethyl or phenyl)

Silicates:-Silicates exist in nature in the form of feldspar, zeolites, mica and asbestos etc.

The basic structure of silicates is SiO_4^{4-}

Zeolites:-Zeolites is a alumino-silicate of metal. Metal cations participating in formation of Zeolite are usually Na^+ , K^+ , or Ca^{2+} .

Zeolites are used to remove permanent hardness of water.

ONE MARK QUESTIONS

1. Why is boron used in nuclear reactions?

Ans:-Because Boron can absorb neutrons.

2. By giving a balanced equation show how $\text{B}(\text{OH})_3$ behaves as an acid in water.



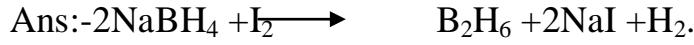
3. Name the element of group 14 which exhibits maximum tendency for catenation?

Ans:-Carbon

4. What is the basic building unit of all silicates?

Ans:- SiO_4^{4-} is the basic unit of all silicates.

5. What happens when NaBH_4 reacts with iodine?



6. What happens when boric acid is heated



7. What is producer gas?

Ans:-Producer gas is a mixture of CO and N_2 in the ratio of 2:1.

8. Write the state of hybridization of 'B' in BF_3 .

ANS:-Hybridisation of 'B' in BF_3 is Sp^2 .

9. Mention the state of hybridization in B in BH_4^- .

Ans:- Sp^3 .

10. Which oxide of carbon is regarded as anhydride of carbonic acid.

Ans:- CO_2 is regarded as a hydride of carbonic acid .



TWO MARKS QUESTIONS

1. Give the chemical reaction as an evidence for each of the following observations.

(i) Tin (II) is a reducing agent whereas lead (II) is not.

(ii) Gallium (I) undergoes disproportionation reaction.

Ans:- (i) Due to inert pair effect Pb^{2+} is more stable than Pb^{4+} . Whereas Sn^{4+} is more stable than Sn^{2+} .



This is because Ga^{3+} is more stable than Ga^+ .

2. What happens when

- (i) Quick lime is heated with coke?
- (ii) Carbon monoxide reacts with Cl_2

Ans:- (i) $Cao + 3C \rightarrow CaC_2 + CO$



3. Give reason

(i) C and Si are always tetravalent but Ge, Sn, Pb show divalency.

(ii) Gallium has higher ionization enthalpy than Al. Explain.

Ans:-(i) Ge, Sn, Pb show divalency due to inert pair effect, Pb^{2+} is more stable than Pb^{4+} .

(ii) Due to poor shielding effect of d-electrons in Ga effective nuclear charge increases as compared to Al thus the I.E is higher than Al.

4. Give reason why boron and aluminium tend to form covalent compounds.

Ans:- Sum of three ionization of both the elements are very high. Thus they have no tendency to lose electrons to form ionic compound. Instead they form covalent compounds.

5. If B-Cl bond has a dipole moment, Explain why BCl_3 molecule has zero dipole moment.

Ans:- B-Cl bond has dipole moment because of polarity. In BCl_3 since the molecule is symmetrical thus the polarities cancel out.

6. Suggest a reason as to why CO is poisonous.

Ans:- CO reacts with haemoglobin to form carboxy-haemoglobin which can destroy the oxygen carrying capacity of haemoglobin and the man dies of suffocation.

7. What do you understand by-

(a) Inert pair effect:- The pair of electron in the valence shell does not take part in bond formation it is called inert pair effect.

(b) Allotropy:- It is the property of the element by which an element can exist in two forms which have same chemical properties but different physical properties due to their structures.

8. How is excessive content of CO_2 responsible for global warming?

Ans:- Excess of CO_2 absorbs heat radiated by the earth. Some of it is dissipated into the atmosphere while the remaining part is radiated back to the earth. Temperature of the earth increases.

9. Describe two similarities and two dissimilarities between B and Al.

Ans:- Similarities:-

- (i) Both have same number of valence electrons.
- (ii) Both have similar electronic configuration.

Dissimilarities:-

- (i) B is a non-metal where Al is a metal
- (ii) B forms acidic oxide whereas Al forms atmospheric oxides.

10. What are fullerenes? How they were prepared?

Ans:- Fullerenes are the allotropes of carbon. Its structure is like a soccer ball.

They are prepared by heating graphite in electric arc in presence of inert gases such as helium or argon.

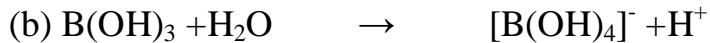
THREE MARKS QUESTIONS

1. What happens when

- (a) Borax is heated strongly

(b) Boric acid is added to water

(c) Aluminium is treated with dilute NaOH



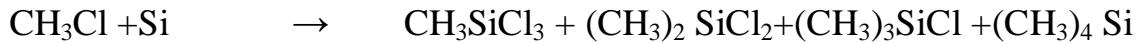
2. Explain the following reactions.

(a) Silicon is heated with methyl chloride at high temperature in the presence of copper.

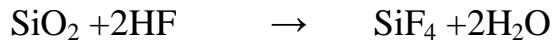
(b) Silicon dioxide is treated with hydrogen fluoride.

(c) CO is heated with ZnO.

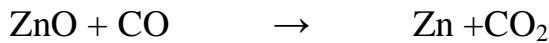
Ans:- (a) A mixture of mono-, di- and trimethylchlorosilanes along with a small amount of tetramethylsilane is formed.



(b) The initially formed silicon tetrafluoride dissolves in HF to form hydrofluorosilicic acid



(c) ZnO is reduced to zinc metal



3. Give reasons:-

(a) Diamond is used as an abrasive.

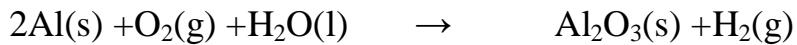
(b) Aluminium alloys are used to make aircraft body.

(c) Aluminium utensils should not be kept in water overnight.

Ans:- (a) Diamond is used as an abrasive because it is an extremely hard substance.

(b) Alloys of aluminium like duralumin is used to make aircraft body due to some of its properties.

(c) Generally aluminium metal does not react with water quickly but when it is kept overnight. It reacts slowly with water in presence of air.

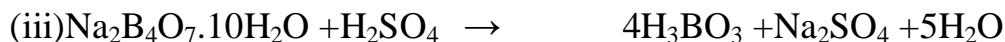


4. A certain salt X, gives the following results.

(i) Its aqueous solution is alkaline to litmus.

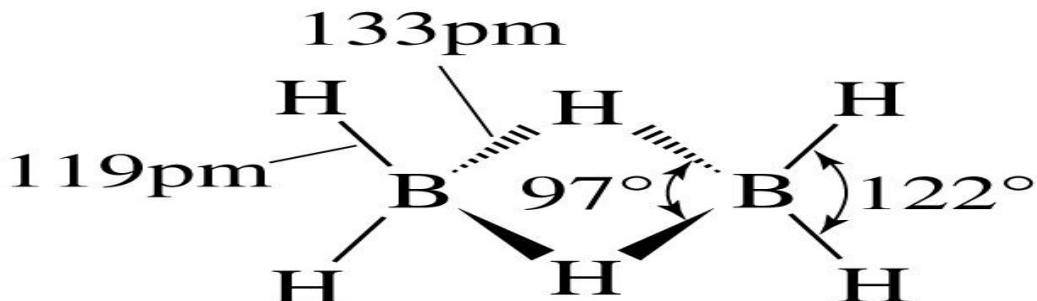
(ii) It swells up to a glassy material Y on strong heating.

(iii) When conc. H_2SO_4 is added to a hot solution of X, white crystal of an acid Z separates out.



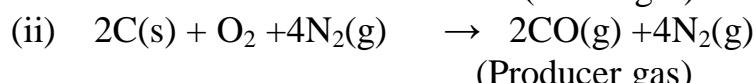
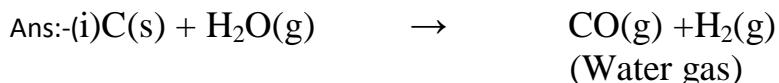
5. Draw structure of diborane.

Ans.

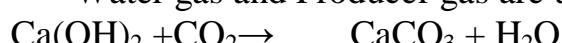


FIVE MARKS QUESTIONS

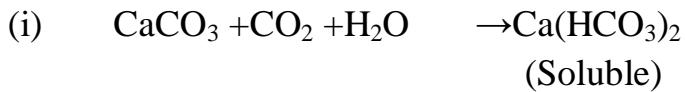
1 Explain the formation of (i) Water gas (ii) Producer gas. Give their uses. What happens when CO_2 is passed through lime water (i) for short duration (ii) for long duration.



Water gas and Producer gas are used as fuel.



(White ppt.)



- 2 (a) Why do Boron halides form addition compound with NH_3 ?
 (b) Assign appropriate reason for each of the following observations :-

- (i) Anhydrous AlCl_3 is used as a catalyst in many organic reactions.
- (ii) No form of elemental silicon is comparable to graphite.

Ans:- (a) It is because BX_3 is electron deficient whereas NH_3 is electron rich.

(b) (i) It is Lewis acid.

(ii) It cannot form $p\pi - p\pi$ bond due to large size.

3. (i) Give reason for the following observations:-

- (a) The tendency for catenation decreases down the group in Group 14.
- (b) The decreasing stability of +3 oxidations state with increasing atomic number in group 13.
- (c) PbO_2 is a stronger oxidizing agent than SnO_2 .
- (d) Molten aluminium bromide is a poor conductor of electricity.

Ans:- (i)(a) It is due to decrease in bond dissociation energy which is due to increase in atomic size.

$\text{C-C} > \text{Si-Si} > \text{Ge-Ge} > \text{Sn-Sn} > \text{Pb-Pb}$.

(b) It is due to inert pair effect.

(c) PbO_2 is stronger oxidizing agent than SnO_2 because Pb^{2+} is more stable than Pb^{4+} whereas Sn^{4+} is more stable than Sn^{2+} .

(d) Molten AlBr_3 is poor conductor of electricity because it is covalent compound.

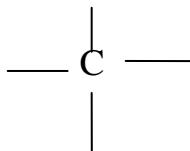
CHAPTER 12

Organic chemistry : Some Basic Principles and Techniques

Organic compounds are the hydrocarbons and their derivatives and organic chemistry is that branch of chemistry that deals with the study of these compounds

Tetravalency of carbon

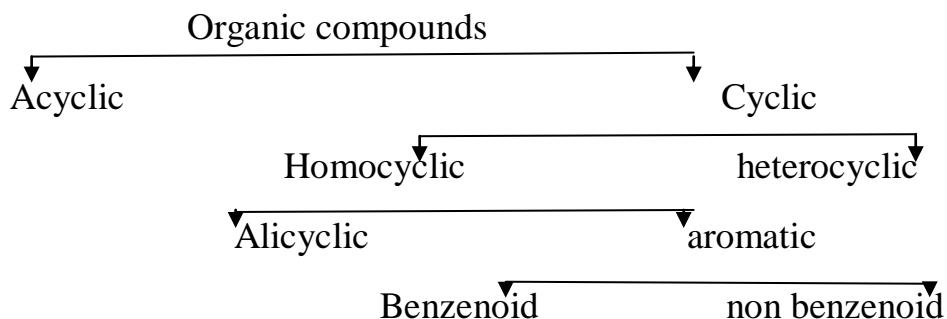
The atomic number of Carbon is 6 and its electronic configuration is 2,4 i.e. it has 4 valence electrons. Thus carbon is always tetracovalent, i.e. it forms 4 covalent bonds with other atoms



Due to tetravalency of carbon it has a tetrahedron shape.

Catenation- The self linking property of carbon is known as catenation. This is the main reason of existence of such large number of compounds

Classification of organic compounds



Functional groups: A functional group may be defined as an atom or a group of atoms present in a molecule which largely determines the chemical properties.

| CLASS OF ORGANIC COMPOUNDS | NAME OF FUNCTIONAL GROUP | STRUCTURE |
|----------------------------|--------------------------|--------------------|
| Alkenes | double bond | =C=C= |
| Alkynes | triple bond | - C ≡ C - |
| Halogens | halogen | - X (F,Cl,Br,I) |
| Alcohols | hydroxyl | -OH |
| Aldehydes | aldehydic(formyl) | -CHO |
| Carboxylic acids | carboxyl | -COOH |
| Acid amides | amides | -CONH ₂ |
| Primary amines | amino | - NH ₂ |

HOMOLOGOUS SERIES

Homologous series is defined as a family or group of structurally similar organic compounds all members of which contain the same functional group, show a gradation in physical and similarity in chemical properties and any two adjacent members of which differ by -CH₂ group. The individual members of this group are called homologues and the phenomenon is called homology.

NOMENCLATURE OF ORGANIC COMPOUNDS

Organic chemistry deals with millions of compounds. In order to clearly identify them, a systematic method of naming known as IUPAC system of nomenclature is adopted. The names are such that the listener can deduce the structure from it. The IUPAC name consists of three parts:

| | Prefix | Word root | Suffix |
|-----|--------|-----------|--------|
| EX: | | 3 methyl | octane |

NOMENCLATURE OF ALKANES

Straight chain alkanes:

The names of such compounds is based on their chain structure, and end with suffix '-ane' and carry a prefix indicating the number of carbon atoms present in the chain.

Branched chain hydrocarbons:

- 1.) The longest carbon chain in the molecule is identified.
- 2.) The numbering is done in such a way that the branched carbon atoms get the lowest possible value.
- 3.) The names of the alkyl groups attached as a branch are then prefixed to the name of the parent alkane and its position is indicated by numbers.
- 4.) The lower number is given to the first in alphabetical order.
- 5.) The carbon atom of the branch that attaches to the root alkane is numbered 1.

Organic compounds having Functional Groups:

The longest chain of carbon atoms containing the functional groups is numbered in such a way that the functional group attached to the carbon atom gets the lowest possible number in the chain.

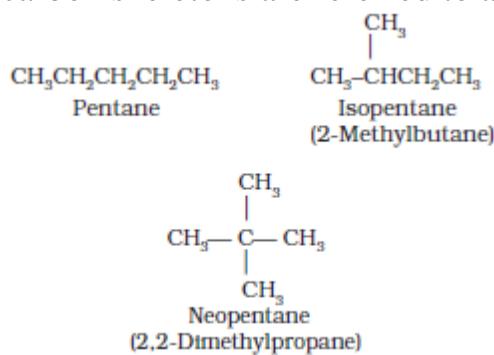
When there are more functional groups then a priority order is followed as:

-COOH, -SO₃H, -COOR, COCl, -CONH₂, -CN, -HC=O, =C=O, -OH, -NH₂, =C=C=, -C≡C-.

ISOMERISM

Two or more compounds having the same molecular formula but different physical and chemical properties are called isomers and this phenomenon is called isomerism.

Chain isomerism: When two or more compounds having same molecular formula but different carbon skeletons are referred to as chain isomers.



Position Isomerism : Compounds which have the same structure of carbon chain but differ in position of double or triple bonds or functional group are called position isomers and this phenomenon is called Position Isomerism. e g



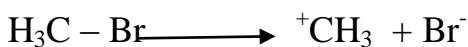
Functional Isomerism : Compounds which have the same molecular formula but different functional group are called functional isomers and this phenomenon is called functional Isomerism. e g



Metamerism: It is due to the presence of different alkyl groups on either side of functional group in the molecule. Ex. $\text{C}_4\text{H}_{10}\text{O}$ represents $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ and $\text{CH}_3\text{OC}_3\text{H}_7$.

FISSION OF COVALENT BOND

Heterolytic cleavage: In this cleavage the bond breaks in such a way that the shared pair of electron remains with one of the fragments.



Homolytic Cleavage: In this cleavage the shared pair of electron goes with each of the bonded atom.



Alkyl free radical

Nucleophiles : A reagent that brings an electron pair is called nucleophile ie nucleus seeking e g $-\text{OH}$, $-\text{CN}$

Electrophiles: A reagent that takes away electron pair is called electrophile I e electron seeking e g $\text{C}=\text{O}$, $\text{R}_3\text{C}-\text{X}$

Inductive Effect: The displacement of the electron along the chain of the carbon atoms due to presence of an atom or group at the end of the chain.

$\delta+++ \delta++ \delta+$



Resonance Effect : The polarity produced in the molecule by the interaction of two pi bonds or between a pi bond and lone pair of electron present on an adjacent atom.

There are two types of resonance effect:

- 1) Positive resonance effect : In this effect the transfer of electrons is away from an atom or substituent group attached to the conjugated system.

The atoms or groups which shows +R effect are halogens, -OH , -OR, -NH₂

- 2) Negative resonance effect : In this effect the transfer of electrons is towards the atom or substituent group attached to the conjugated system.

The atoms or groups which shows -R effect are -COOH , -CHO , -CN

METHODS OF PURIFICATION OF ORGANIC COMPOUNDS :

Sublimation : This method is used to separate the sublimable compounds from non sublimable compounds.

Crystallisation: This method is based on the difference in the solubilities of compound and impurities in a suitable solvent. The impure compound is dissolved in solvent at heated at higher temp .on cooling the hot and conc solution pure compounds crystallizes out.

Distillation: This method is used to separate volatile liquids from non volatile liquids and liquids having sufficient difference in their boiling points.

Fractional distillation: If the boiling points of two liquids is not much , they are separated by this method.

Distillation under reduced pressure : This method is used to purify liquids having high boiling points and decomposes at or below their boiling points.

Steam distillation : This method is used to separate substances which are steam volatile and are immiscible with water.

Differential Extraction: When an organic compound is present in an aqueous medium it is separated by shaking it with organic solvent in which it is more soluble than in water. The aqueous solution is mixed with organic solvent in a separating funnel and shaken for sometimes and then allowed to stand for some time .when organic solvent and water form two separate layers the lower layer is run out by opening the tap of funnel and organic layer is separated. the process is repeated several times and pure organic compound is separated.

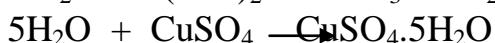
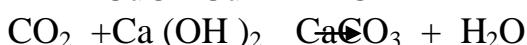
Chromatography :This technique is used to separate mixtures in to their components ,purify the compounds and test the purity of compounds.It is classified as

Adsorption Chromatography : It is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Silica jel or alumina is used as adsorbents.

Partition Chromatography : It is based on the continuous differential portioning of components of a mixture between stationary and mobile phase.

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

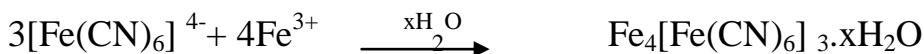
Detection of Carbon and Hydrogen: The Carbon and Hydrogen present in the Organic compound is detected by heating the compound with Copper II oxide in a hard glass tube when carbon present in the compound is oxidized to CO₂ which can be tested with lime Water and Hydrogenis converted to water which can be tested with anhydrous copper sulphate which turns blue.



DETECTION OF OTHER ELEMENTS

Sodium Fusion Extract: A small piece of dry Sodium metal is heated with a organic compound in a fusion tube for 2 -3 minutes and the red hot tube is plunged in to distilled water contained in a china dish. The contained of the china dish is boiled ,cooled and filtered. The filtrate is known as Sodium fusion extract.

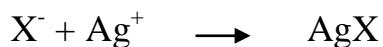
Test for Nitrogen : The sodium fusion extract is boiled with iron II sulphate and then acidified with Concsulphuric acid , the formation of Prussian blue colour confirms the presence of nitrogen.



Test for Sulphur: the sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur. $S^{2-} + Pb^{2+} \longrightarrow PbS$

Black

Test for halogens: The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish ppt. sparingly soluble in ammonium hydroxide shows the presence of bromine, a yellowish ppt. insoluble in ammonium hydroxide shows the presence of iodine.



QUANTITATIVE ANALYSIS(Carbon and Hydrogen)

Let the mass of organic compound be m g. Mass of water and carbon dioxide produced be m_1 and m_2 g respectively;

$$\% \text{ of carbon} = \frac{12 \times m_2 \times 100}{44 \times m}$$

$$\% \text{ of hydrogen} = \frac{2 \times m_1 \times 100}{18 \times m}$$

Nitrogen

DUMAS METHOD: A known mass of organic compound is heated with excess of CuO in an atmosphere of CO₂, when nitrogen of the organic compound is converted into N₂ gas. The volume of N₂ thus obtained is converted into STP and the percentage of nitrogen determined by applying the equation:

$$\text{Volume of Nitrogen at STP} = \frac{P_1 V_1 \times 273}{760 \times T_1}$$

$$\% \text{N} = \frac{28 \times \text{vol of N}_2 \text{ at STP} \times 100}{22400 \times \text{mass of the substance taken}}$$

KJELDAHL'S METHOD: A known mass of organic compound is heated with conc. H₂SO₄ in presence of K₂SO₄ and little CuSO₄ or Hg in a long necked flask called Kjeldahl's flask when nitrogen present in the organic compound is quantitatively converted into (NH₄)₂SO₄. (NH₄)₂SO₄ thus obtained is boiled with excess of NaOH solution to liberate NH₃ gas which is absorbed in a known excess of a standard acid such as H₂SO₄ or HCl.

The vol of acid unused is found by titration against a standard alkali solution. From the vol of the acid used, the percentage of nitrogen is determined by applying the equation,

$$\% \text{N} = \frac{1.4 \times \text{Molarity of the acid} \times \text{Basicity of the acid} \times \text{Vol of the acid used}}{\text{Mass of the substance taken}}$$

Halogens

Carius method:

A known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass test tube known as carius tube in a furnace. Carbon and hydrogen present in the compound are oxidized to carbon dioxide and water. The halogen present forms the corresponding silver halide. It is filtered, dried, and weighed.

Let the mass of the organic compound taken = m g

Mass of AgX formed = m₁ g

1 mol of AgX contains 1 mol of X

Mass of halogen in m₁ g of AgX

$$= \frac{\text{at mass of X } xm_1 \text{ g}}{\text{Molecular mass of AgX}}$$

% of halogen

$$= \frac{\text{at mass of X } xm_1 \text{ g} \times 100}{\text{Molecular mass of AgX} \times m} \%$$

Sulphur

Let the mass of the organic compound taken = m g

Mass of BaSO₄ formed = m₁ g

$$\% \text{ of sulphur} = \frac{32 \times m_1 \times 100}{233 \times m} \%$$

Phosphorous

Let the mass of the organic compound taken = m g

Mass of ammonium phosphomolydate = m₁ g

$$\% \text{ of phosphorous} = \frac{31 \times m_1 \times 100}{1877 \times m} \%$$

Oxygen

Let the mass of the organic compound taken = m g

Mass of CO₂ = m₁ g

$$\% \text{ of oxygen} = \frac{32 \times m_1 \times 100}{44 \times m} \%$$

One Mark Questions

Q1 Suggest a method to purify a liquid which decomposes at its boiling point.

A 1 The process Distillation Under reduced pressure is used to purify a liquid which decomposes at its boiling point.

Q 2 How will you separate a mixture of O-nitrophenol and p- nitrophenol ?

A 2 O-nitrophenol is steam volatile therefore it can be separated by Steam distillation.

Q 3 Lassaigne's test is not shown by diazonium Salt. Why?

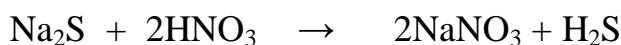
A 3 On heating diazonium Salts loses Nitrogen and could not fuse with the Sodium metal therefore diazonium Salt do not show Positive Lassaigne's test for nitrogen.

Q 4 Alcohols are weaker acids than Water, Why ?

A 4 The alkyl group in alcohols has + I effect due to which electron density is increases on Oxygen atom which makes the release of hydrogen ion more difficult from alcohol. $R - \rightarrow O - H$

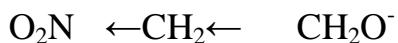
Q 5 Why is nitric acid is added to Sodium extract before adding Silver nitrate for testing halogens ?

A 5 Nitric acid is added to decompose NaCN and Na₂S



Q 6 which of the two $\text{O}_2\text{NCH}_2\text{CH}_2^-$ or $\text{CH}_3\text{CH}_2\text{O}^-$ is expected to be more stable and why ?

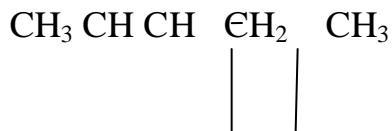
A 6 NO₂ group has -I effect and disperse the negative charge on Oxygen atom



Q 7 Arrange the following in increasing Order of Stability ;



Q 8 Write the IUPAC name of the following

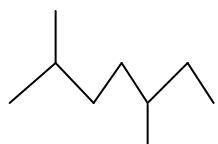


A 8 2,3Dimethylpentane

Q 9 Write the hybridized state of C atoms in the following



Q 10 Give the IUPAC name of the following compound.



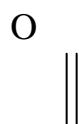
A 10 2,5Dimethylheptane

Two Marks Questions

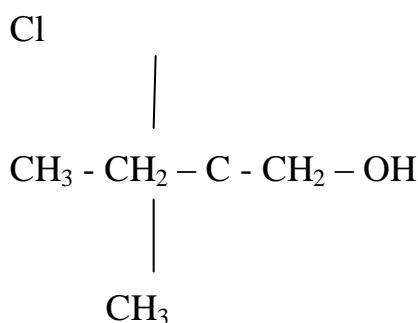
Q 1 Draw the Structures of the following compounds.

- A) Hex-3-enoic acid b) 2-chloro-2-methylbutan-1-ol

A 1 a)

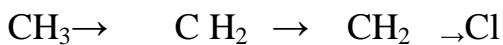
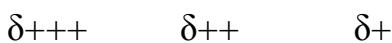


b)



Q 2 Explain Inductive effect with example.

A 2 Inductive Effect: The displacement of the electron along the chain of the carbon atoms due to presence of an atom or group at the end of the chain.



Q 3 Explain why $(\text{CH}_3)_3\text{C}^+$ is more stable than $\text{CH}_3\text{C}^+\text{H}_2$.

A 3 $(\text{CH}_3)_3\text{C}^+$ has nine alpha hydrogens and has nine hyperconjugation structures while $\text{CH}_3\text{C}^+\text{H}_2$ has three alpha hydrogens and has three hyperconjugation structures, therefore $(\text{CH}_3)_3\text{C}^+$ is more stable than $\text{CH}_3\text{C}^+\text{H}_2$

Q 4 Give the number of Sigma and pi bonds in the following molecules

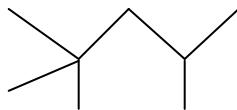
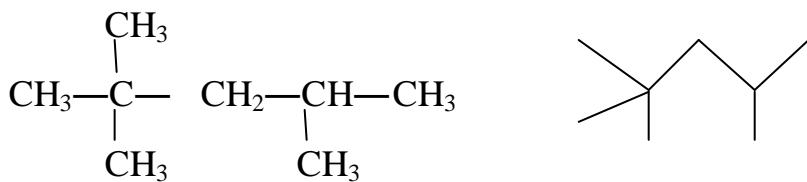
- a) CH_3NO_2 b) HCONHCH_3

A 4 a) 6 Sigma and 1 pi bond

- b) 8 Sigma and 1 pi bond

Q 5 Write the condensed and bond line formula of 2,2,4-Trimethylpentane.

A 5



Q 6 How Sodium fusion extract is prepared ?

A 6 A small piece of dry Sodium metal is heated with a organic compound in a fusion tube for 2 -3 minutes and the red hot tube is plunged in to distilled water contained in a china dish. The contained of the china dish is boiled ,cooled and filtered. The filtrate is known as Sodium fusion extract.

Q 7 Explain the principle of paper chromatography.

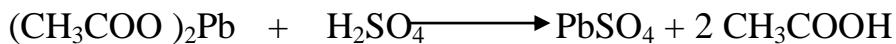
A 7 Paper chromatography is based on the difference in the rates at which the components of a mixture are adsorbed. The material on which different components are adsorbed is called Stationary phase which is generally made up of alumina, silica jel or activated charcoal. The mixture to be separated is dissolved in a suitable medium and it is called moving phase. The moving phase is run on the Stationary phase , the different compounds are adsorbed on stationary phase at different rates.

Q 8 Why is an organic compound fused with Sodium for testing nitrogen,halogens and sulphur ?

A 8 On fusing with sodium metal the elements presents in an organic compounds are converted in to sodium salts which are water soluble which can be filtered and detected by the respective tests.

Q 9 It is not advisable to use sulphuric acid in place of acetic acid for acidification while testing sulphur by lead acetate test. Give reason

A 9 Lead acetate on reacting with sulphuric acid will give a white ppt of lead sulphate which interfere in the detection of sulphur.



Q 10 Under what conditions can the process of steam distillation is used ?

A 10 Steam distillation is used to purify the liquids which are steam volatile and water and the liquid are not miscible with each other.

Three Marks Questions

Q 1 In an estimation of sulphur by carius method 0.468 g of an organic compound gave 0.668 g of barium sulphate. Find the percentage of sulphur in the compound.

A 1 Mass of the compound = 0.468 g

Mass of the barium sulphate = 0.668 g

% of sulphur = $\frac{32 \times \text{Mass of barium sulphate} \times 100}{233 \times \text{Mass of the compound}}$

$$= \frac{32 \times 0.668 \times 100}{233 \times 0.468}$$

$$= 19.60 \%$$

Q 2 Which bond is more polar in the following pairs of molecules.

a) H₃C-H, H₃C-Br b) H₃C-NH₂, H₂C-OH c) H₃C-OH, H₃C-SH

A 2 a) C-Br because Br is more electronegative than H

- b) C-O because O is more electronegative than N
c) C-O because O is more electronegative than S

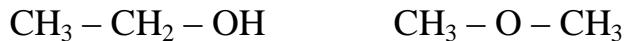
Q 3 Define Isomerism.Explain position Isomerism and Functional Isomerism with examples.

A 3 Two or more compounds having the same molecular formula but different physical and chemical properties are called isomers and this phenomenon is called isomerism.

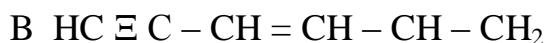
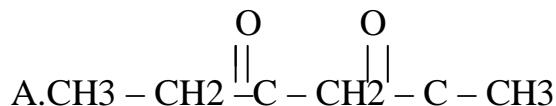
Position Isomerism : Compounds which have the same structure of carbon chain but differ in position of double or triple bonds or functional group are called position isomers and this phenomenon is called Position Isomerism. e g



Functional Isomerism :Compounds which have the same molecular formula but different functional group are called functional isomers and this phenomenon is called functional Isomerism. e g



Q 4 write the IUPAC names of the following compounds.



A 4 A hexane 2,4dione

- B hexa-1,3-dien-5-yne
 C 1-bromo-4-chlorobutane

Q 5 Define Homologous series. Write the general formula of alkane, alkene and alkynes.

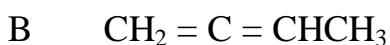
A 5 Homologous Series : It is defined as group of similar organic compounds which contains the similar functional groups and the two adjacent members of the series differ by a --CH_2 group.

Alkanes $\text{C}_n\text{H}_{2n+2}$

Alkenes C_nH_{2n}

Alkynes $\text{C}_n\text{H}_{2n-2}$

Q 6 How many Sigma and pi bonds are present in the following molecules .



A 6 A Sigma bonds = 10 pi bonds = 3

B Sigma bonds = 9 pi bonds = 2

Q 7 Define functional groups. Write the general formula of Carboxylic acids acid chlorides.

A 7 Functional Groups :It is an atom or group of atoms bonded together in a unique manner which is usually the site of chemical reactivity in an organic molecule. e g CH_3OH

General formula of Carboxylic acids : $\text{C}_n\text{H}_{2n+1}\text{COOH}$

General formula of acid chlorides : RCOCl

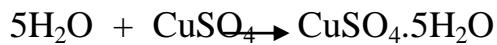
Q 8 Write a short note on differential extraction.

A 8 When an organic compound is present in an aqueous medium it is separated by shaking it with organic solvent in which it is more soluble than in water. The aqueous solution is mixed with organic solvent in a separating funnel and shaken for sometimes and then allowed to stand for some time .when organic solvent and water form two separate layers the lower layer is run out by opening the tap of funnel and organic layer is separated. the process is repeated several times and pure organic compound is separated.

Q 9 How carbon and Hydrogen is detected in a organic compounds.

A 9 The Carbon and Hydrogen present in the Organic compound is detected by heating the compound with Copper II oxide in a hard glass tube when carbon present

in the compound is oxidized to CO₂ which can be tested with lime Water and Hydrogenis converted to water which can be tested with anhydrous copper sulphate which turns blue.



Q 10 Write a short note on Resonance effect .

Resonance Effect : The polarity produced in the molecule by the interaction of two pi bonds or between a pi bond and lone pair of electron present on an adjacent atom.

There are two types of resonance effect:

1. Positive resonance effect: In this effect the transfer of electrons is away from an atom or substituent group attached to the conjugated system.
The atoms or groups which shows +R effect are halogens,-OH , -OR,-NH₂
2. Negative resonance effect: In this effect the transfer of electrons is towards the atom or substituent group attached to the conjugated system.

The atoms or groups which shows -R effect are -COOH , -CHO , -CN

Five Marks Questions

Q 1 Differentiate between the principle of estimation of nitrogen in an organic compound by i) Dumas method ii) Kjeldahl's method.

Ans: DUMAS METHOD: A known mass of organic compound is heated with excess of CuO in an atmosphere of CO₂, when nitrogen of the organic compound is converted into N₂ gas. The volume of N₂ thus obtained is converted into STP and the percentage of nitrogen determined by applying the equation:

$$\text{Volume of Nitrogen at STP} = \frac{P_1 V_1 \times 273}{760 \times T_1}$$

$$\%N = \frac{28 \times \text{vol of N}_2 \text{ at STP} \times 100}{22400 \times \text{mass of the substance taken}}$$

KJELDAHL'S METHOD: A known mass of organic compound is heated with conc. H₂SO₄ in presence of K₂SO₄ and little CuSO₄ or Hg in a long necked flask called Kjeldahl's flask when nitrogen present in the organic compound is quantitatively converted into (NH₄)₂SO₄. (NH₄)₂SO₄ thus obtained is boiled with excess of

NaOH solution to liberate NH₃ gas which is absorbed in a known excess of a standard acid such as H₂SO₄ or HCl.

The vol of acid unused is found by titration against a standard alkali solution. From the vol of the acid used, the percentage of nitrogen is determined by applying the equation,

$$\frac{\%N = 1.4 \times \text{Molarity of the acid} \times \text{Basicity of the acid} \times \text{Vol of the acid used}}{\text{Mass of the substance taken}}$$

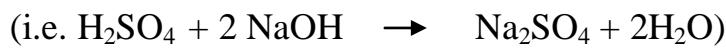
Q 2 A sample of 0.50g of organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50mL of 0.5M H₂SO₄. The residual acid required 60mL of 0.5M solution of NaOH for neutralization. Find the percentage composition of nitrogen in the compound.

Ans: the vol of H₂SO₄ used.

Vol of acid taken=50mL of 0.5M H₂SO₄= 25mL of 1M H₂SO₄

Vol of alkali used for neutralization of excess acid= 60 mL of 0.5M NaOH=30mL of 1M NaOH

Now 1 mole of H₂SO₄ neutralizes 2 moles of NaOH



... 30 mL of 1M NaOH = 15mL of 1M H₂SO₄

% of nitrogen.

1 mole of H₂SO₄ neutralizes 2 moles of NH₃ ... 10mL of 1M H₂SO₄ = 20mL of 1M NH₃

But 1000mL of 1M NH₃ contain N=14g.

$$20 \text{ ml of 1M NH}_3 \text{ will contain nitrogen} = \frac{14 \times 20}{1000}$$

But this amount of nitrogen is present in 0.5 g of organic compound

$$\therefore \% \text{ of N} = \frac{14 \times 20 \times 100}{1000 \times 0.5} = 56.0$$

Q 3 You have a mixture of three liquids A, B , C. there is a large difference in the boiling point of A and the rest two liquids. Boiling points of liquids B and C are quite close. Liquid A boils at higher temperature than B and C and boiling point of B is lower than C. How will you separate the components of the mixture.

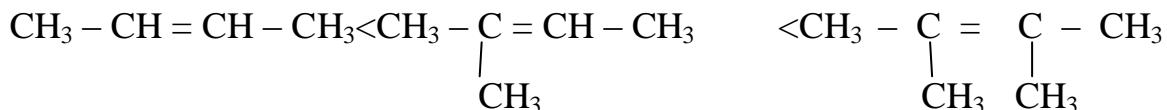
Ans Since the boiling point of liquid A is much higher than those of liquids B and C , therefore separate liquid A by simple distillation. Since boiling points of liquids B and C are quite close but much lower than liquid A therefore mixture of B and C will distil together leaving behind A. on further heating A will distil over.

Now place the mixture of liquids B and C in a flask fitted with fractionating column. Since the b.p. of liquid B is lower than that of C , on fractional distillation first liquid B will distil over and then liquid C.

HOTS QUESTIONS

Q 1 Explain hyperconjugation effect. How does hyperconjugation effect explain the stability of alkenes?

Ans The relative stability of various classes of carbonium ions may be explained by the number of no-bond resonance structures that can be written for them. Such structures are obtained by shifting the bonding electrons from an adjacent C-H bond to the electron deficient carbon so the positive charge originally on carbon is dispersed to the hydrogen. This manner of electron release by assuming no bond character in the adjacent C-H bond is called Hyperconjugation. Greater the hyperconjugation greater will be the stability of alkenes.



Q 2 In DNA and RNA nitrogen is present in the ring system. Can kjeldahl method be used for the estimation of nitrogen present in these ?give reasons

Ans In DNA and RNA nitrogen is present in heterocyclic rings. Kjeldahl method can not be used to estimate nitrogen present in the ring because cannot be completely converted into $(\text{NH}_4)_2\text{SO}_4$ during digestion. Therefore Kjeldahl method can not be used to estimate nitrogen present in DNA and RNA.

Q 3 1.216 g of an organic compound was Kjeldahlied and the ammonia evolved was absorbed in 100 mL 1N H_2SO_4 . The remaining acid solution was made upto 500ml by addition of water. 20ml of this dilute solution required 32mL of N/10 caustic soda solution for complete neutralization. Calculate the percentage of nitrogen in the organic compound.

Ans 20 ml of dil. Unreacted H_2SO_4 = 32mL of N/10 NaOH sol.

$$500 \text{ ml of dil unreacted } \text{H}_2\text{SO}_4 = \frac{32 \times 500 \text{ mL of NNaOH}}{20 \text{ } \frac{10}{20 \times 10}} = 80 \text{ mL 1 N NaOH}$$

But 80ml 1 N NaOH = 80ml 1 N NaOH So, acid left unused = 80ml 1 N H₂SO₄

Acid used = (100 - 80) = 20ml 1 N H₂SO₄

$$\%N = \frac{1.4 \times \text{Normality of the acid} \times \text{Vol of the acid used}}{\text{Mass of the substance taken}}$$

$$= \frac{1.4 \times 1 \times 20}{1.216}$$

$$= 23.026$$

CHAPTER 13

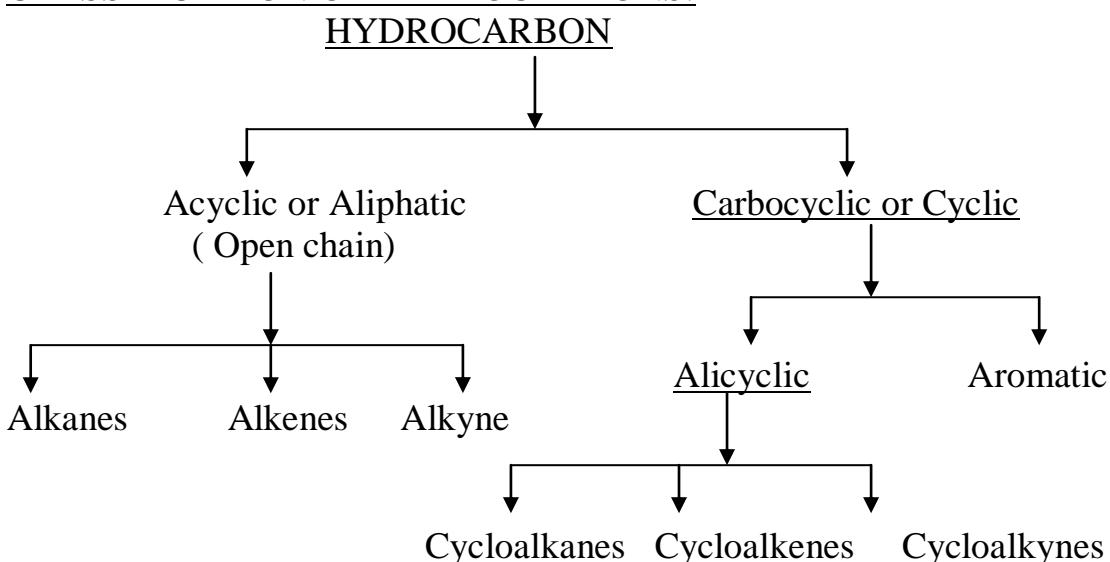
HYDROCARBON

- Hydrocarbons are composed of Carbon and hydrogen.
- The important fuels like Petrol, kerosene, coal gas, CNG, LPG etc. are all hydrocarbons or their mixture.

Sources:

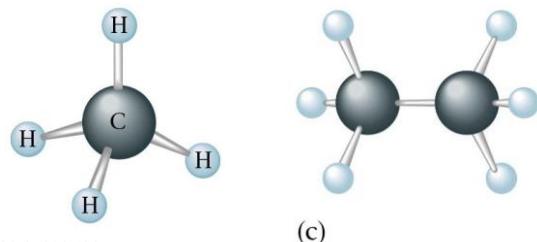
Petroleum and natural gas are the major sources of aliphatic hydrocarbon while coal is an important source of aromatic hydrocarbons. The oil trapped inside the rocks is known as petroleum. PETRA – ROCK, OLEUM – OIL. The oil in the petroleum field is covered with a gaseous mixture known as natural gas. The main constituents of the natural gas are methane, ethane, propane and butane.

CLASSIFICATION OF HYDROCARBONS:



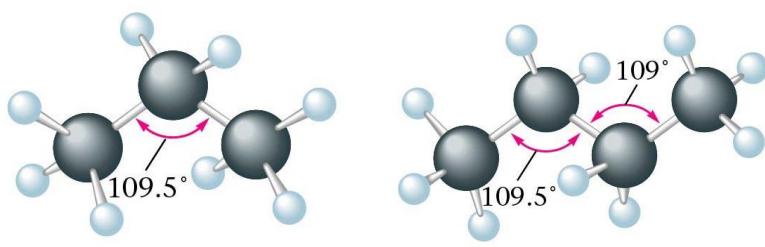
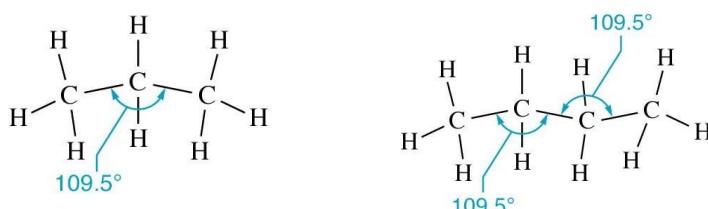
Alkanes:-

- Paraffins
- General formula C_nH_{2n+2}
- sp^3 hybridisation
- C–C bond length $1.15\text{ }4\text{ \AA}^0$
- Chemically unreactive
- Show chain, position and optical isomerism.
- Heptane has 9 isomer, Octane 18 and Decane 75.



(c)

Nomenclature:

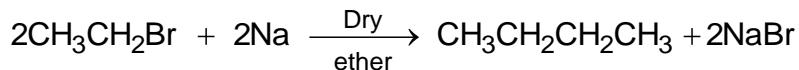


(a) Propane

(b) Butane

Preparation:-

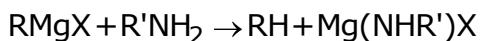
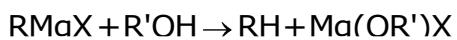
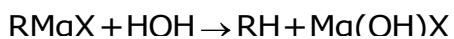
① Wurtz reaction:-



- Follow mainly free radical mechanism
 - Useful in preparing an alkane containing even number of carbon atoms
 - Stepping up reaction
- Frankland reaction

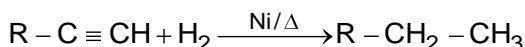


② From Grignard reagent (RMgX)



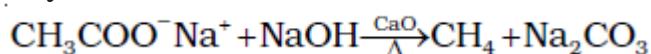
③ From unsaturated hydrocarbons:-

Sabatier-Senderens reduction



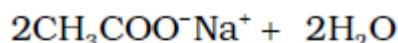
4. From carboxylic acids-

Decarboxylation.-



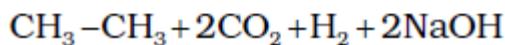
Sodium ethanoate

Kolbe's electrolytic method-



Sodium acetate

↓ Electrolysis



❖ Physical Properties:-

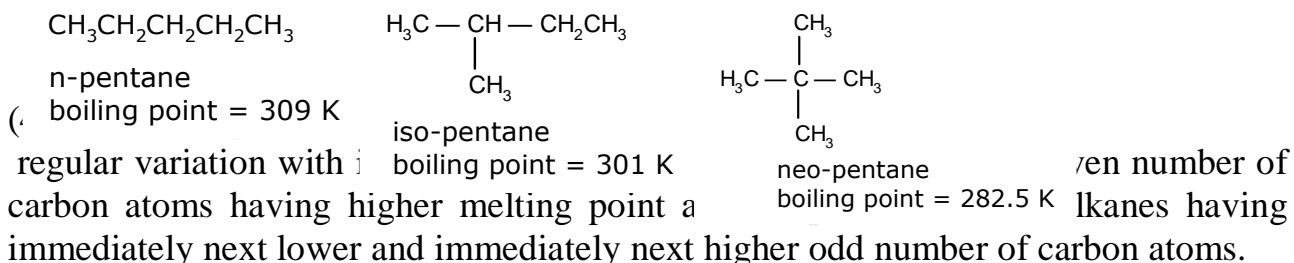
- (1) Nature:- Non-Polar due to covalent nature of C—C bond and C—H bond. C—C bond energy = 83 kJ/mole and C—H bond energy = 99 kJ/mole.
 C_1-C_4 = gases, C_5-C_{17} = colourless odourless liquid and $>\text{C}_{17}$ = Solid.
- (2) Solubility:- Like dissolve like
Viz, Polar compounds dissolve in polar solvent and Non-Polar compound dissolve in non polar solvent.
- (3) Boiling point:- Low boiling point due to non polar in nature.

The molecules are held together only by weak Van der Waals' forces.

Since we know that the magnitude of Van der Waals' forces is directly proportional to the molecular size. Therefore, the boiling point increases with increase the molecular size i.e. with increase in number of carbon atoms.

Noted:- the boiling points of the branched chain Alkanes are less than the straight chain isomers.

This is due to the fact that branching of the chain makes the molecule more compact and thereby decreases the surface area and consequently, the magnitudes of Van der Waals' forces also decrease.

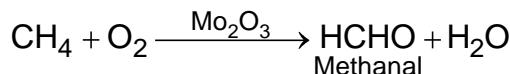
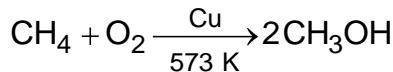


❖ Chemical properties

① Combustion:- $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

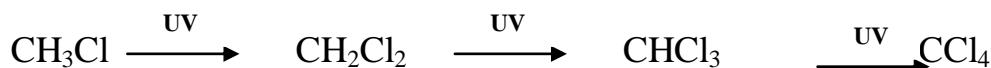
$$\Delta H = -217.0 \text{ K cal/mole}$$

② Oxidation:-

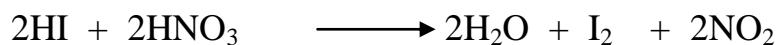


③ Substitution:-

① Halogenation:-

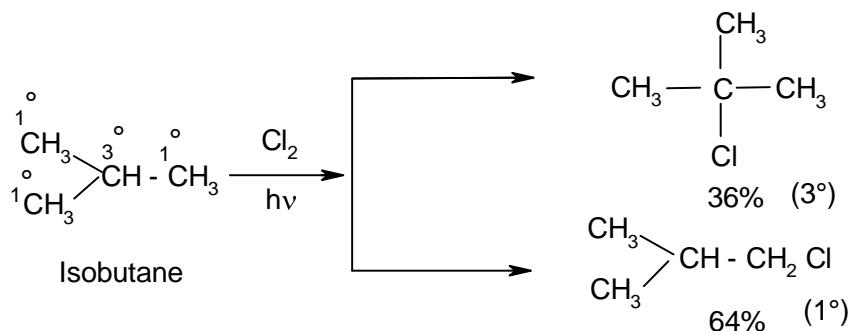
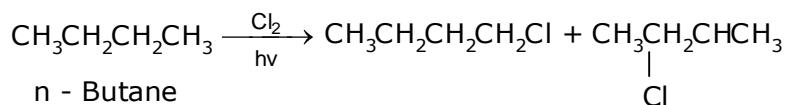


Noted:- Iodination is a reversible reaction. So it is carried out by heating alkane in the presence of some oxidizing agent like iodic acid (HIO_3) or nitric acid (HNO_3) or mercuric oxide (HgO) which oxidizes HI formed during the reaction.



Noted:- Fluorination of alkane takes place explosively resulting even in the rupture of C—C bond in higher alkanes.

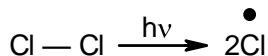
- Features of Halogenations:-
- (i) The reactivity of Halogens:- $F_2 > Cl_2 > Br_2 > I_2$.
- (ii) The rate of replacement of Hydrogens of alkanes is:
 $3^\circ > 2^\circ > 1^\circ$



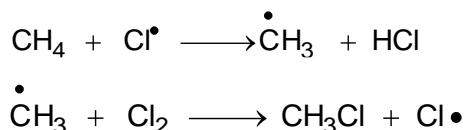
Mechanism:- halogenations reaction take place by free radical mechanism. The reaction proceeds in the following steps:

Initiation

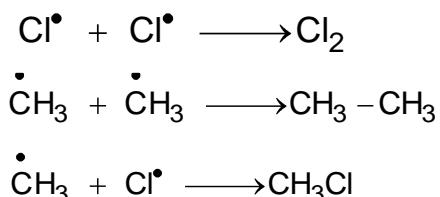
- (i) Chain initiation step:-



- (ii) Chain Propagation step:-

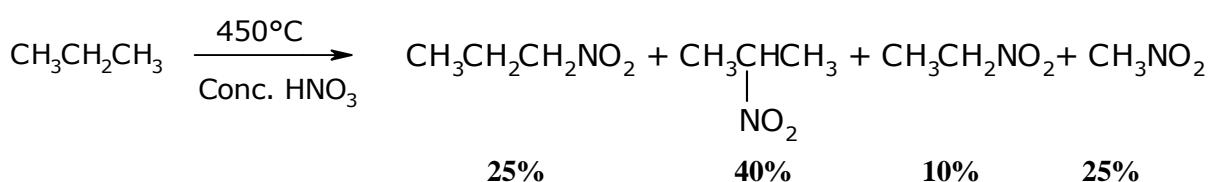


- (iii) Chain Termination step:-

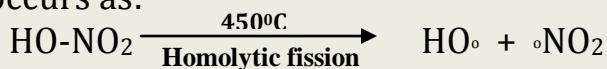


② Nitration:-

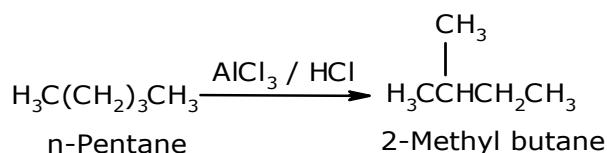
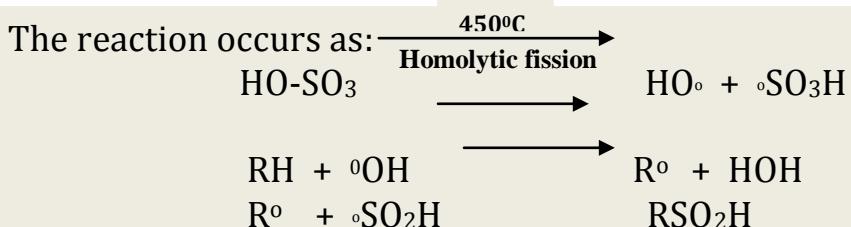
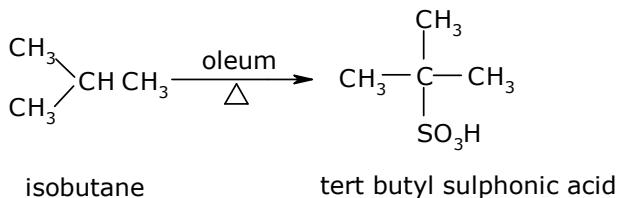
- ☞ The reaction takes places by free radicals mechanism at high temp ($450^\circ C$).
- ☞ At high temp C—C bond is also broken so that mixture of nitroalkanes is obtained.



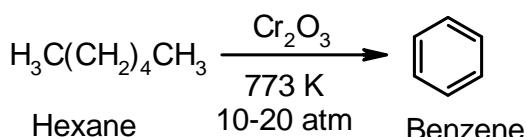
The reaction occurs as:



③ Sulphonation:- replacement of hydrogen atom of alkane by $-\text{SO}_3\text{H}$ group.



⑤ Aromatization:-



This method is also called dehydrogenation or hydroforming

Similarly, heptane gives toluene, n-Octane give o-xylene and 2, methyl heptane give m-xylene.

⑥ Thermal decomposition or Pyrolysis or cracking or Fragmentation: - when higher alkanes are heated at high temp (about 700-800k) in the presence of alumina or silica catalysts, the alkanes break down to lower alkanes and alkenes.

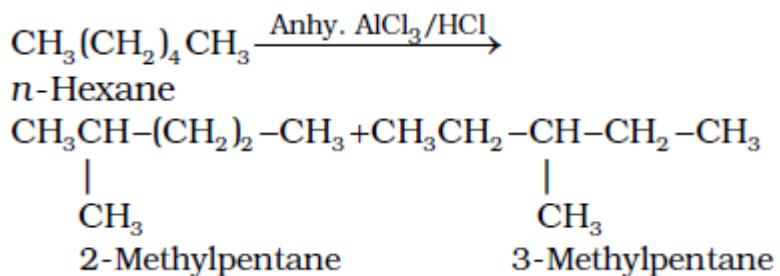


⑦ Action of steam:- catalyst: nickel, alumina Al_2O_3



This reaction is used for the industrial preparation of hydrogen from natural gas.

8. Isomerisation:-

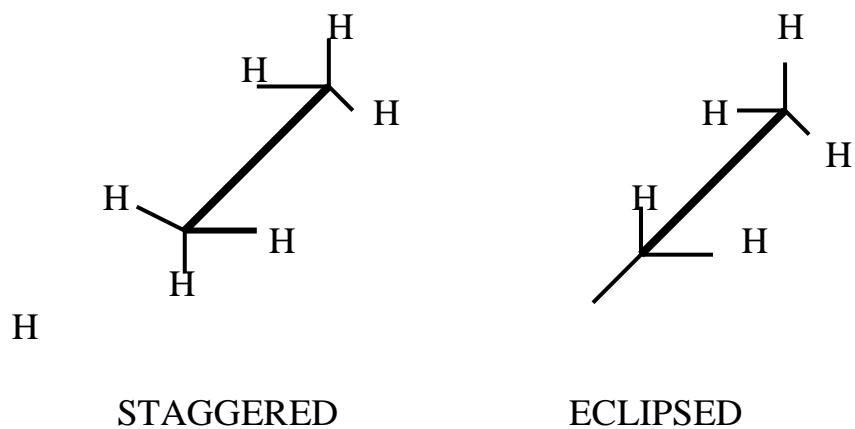


❖ CONFORMATIONAL ISOMERISM:

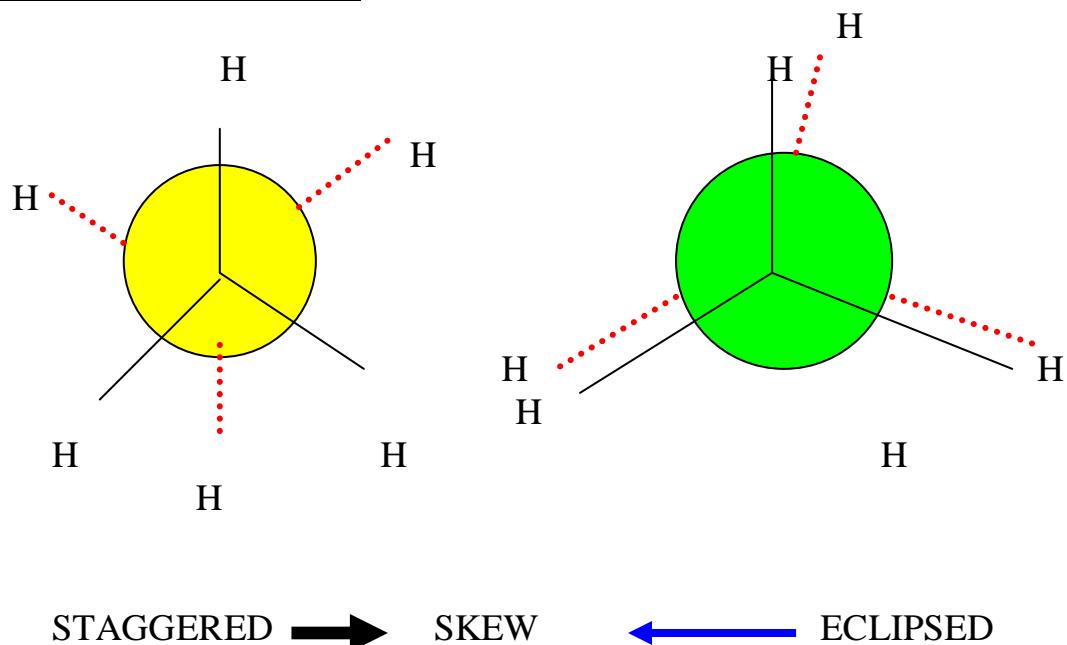
The different molecular arrangements arising as a result of rotation around carbon-carbon single bonds are called conformational isomers or rotational isomers and the phenomenon is called conformational isomerism.

Numerous possible arrangements of ethane are possible. Two extreme conformations are known. These are eclipsed conformation and staggered conformation.

SAWHORSE REPRESENTATION

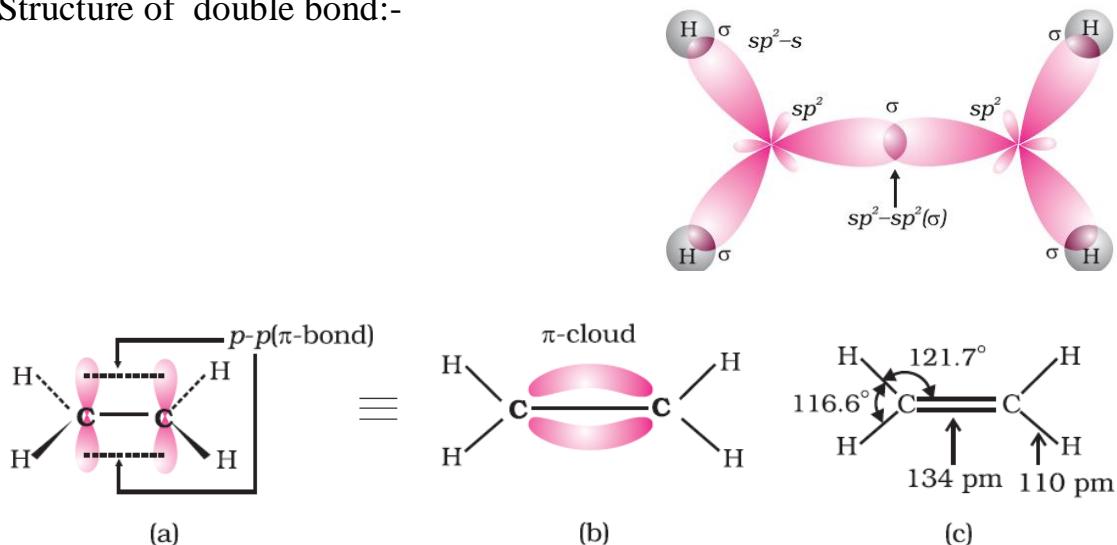


NEWMAN PROJECTION



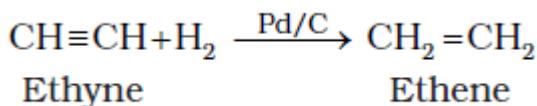
Alkenes

- Unsaturated hydrocarbon which have double bond.
- General molecular formula C_nH_{2n}
- $C-C$ bond hybridization 1.34 \AA^0
- sp^2 hybridization
- When we treated Alkene with chlorine, oily products are obtained. So Alkenes are also known as Olefins. (Greek oleifiant meaning oil forming).
- Show chain, positional and geometrical isomerism
- Structure of double bond:-

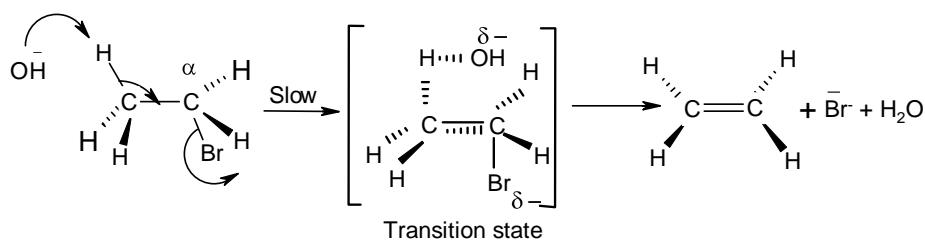
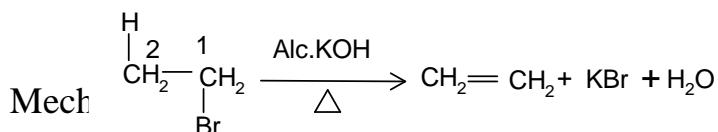


❖ Preparation:-

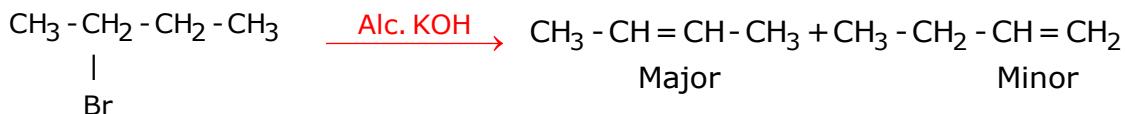
- From Alkynes:- Alkynes on partial reduction with Partially deactivated palladised charcoal known as *Lindlar's catalyst* give alkynes.



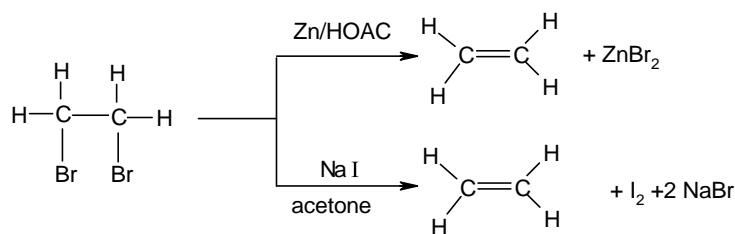
- From Haloalkanes: - dehydrohalogenation
(E_2 or 1,2-elimination or Bita-elimination)



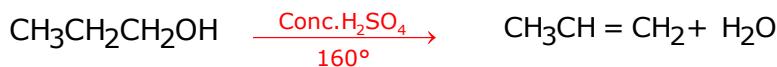
- predominant formation of a substituted alkene is formed according to Saytzeff's rule



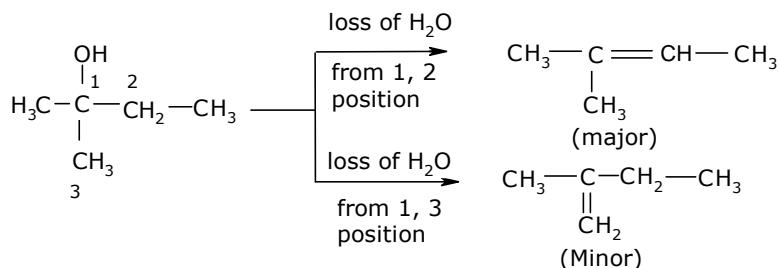
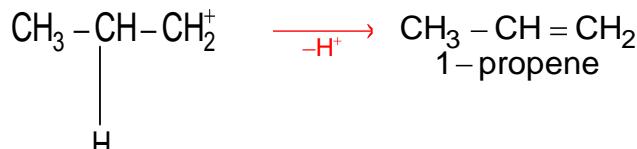
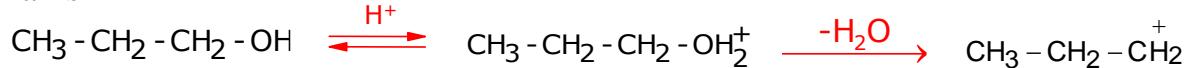
3. From Dihaloalkanes: - dehalogenation



4. From Alcohols:- Dehydration (E1 - elimination)



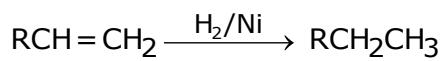
Mechanism



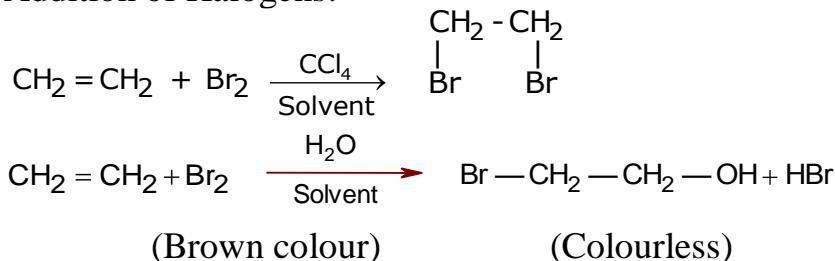
❖ Chemical Properties:-

① Addition Reaction:- Alkene show electrophilic addition reaction.

1. Addition of Hydrogen:-

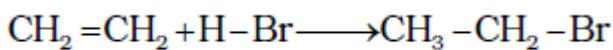


2. Addition of Halogens:-



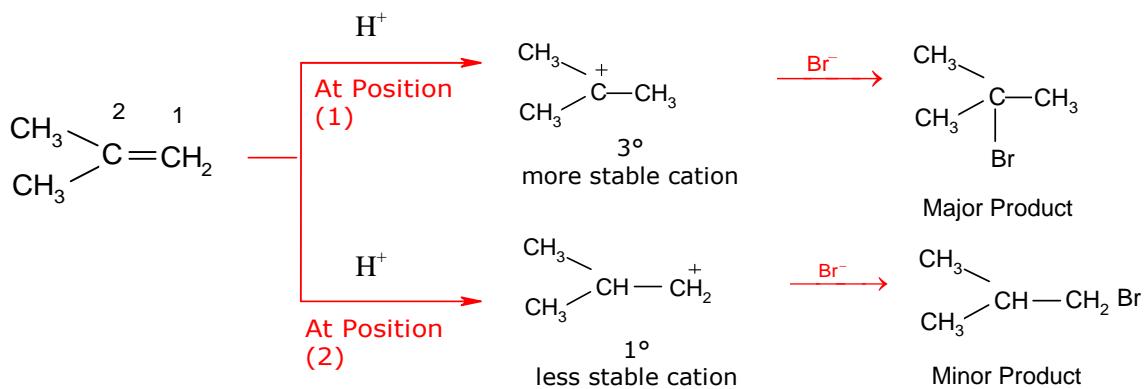
3. Addition of hydrogen halides-

Addition reaction of HBr to symmetrical alkenes

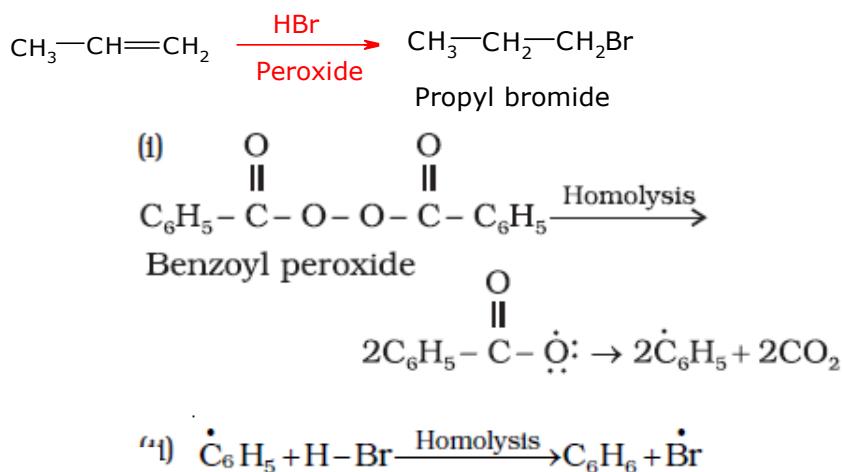


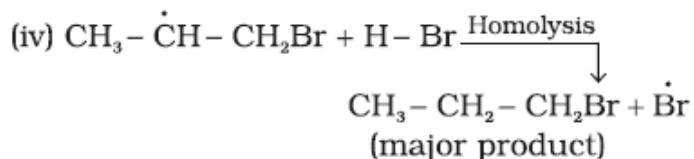
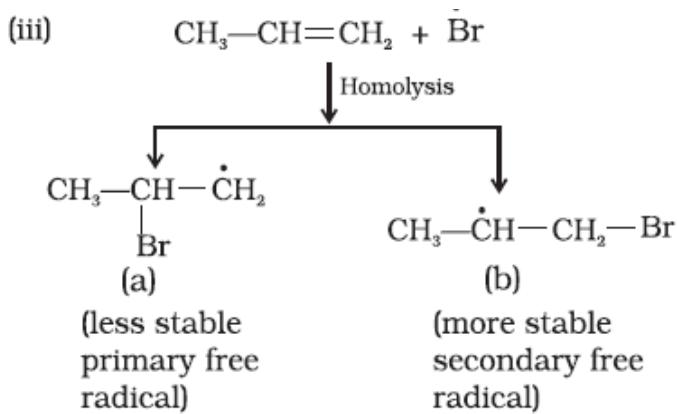
Addition reaction of HBr to unsymmetrical alkenes takes place according to Markovnikov Rule

Markownikov rule:- negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms. e.g



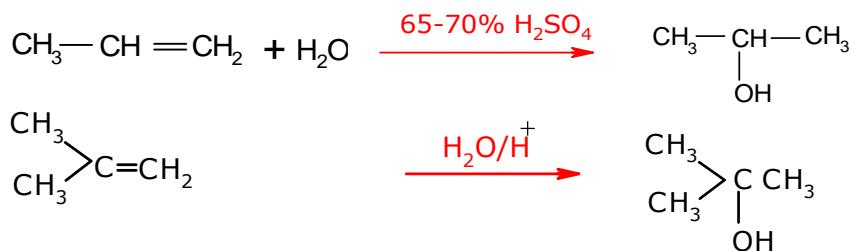
Peroxide effect or Kharasch (Anti Markownikoff's addition):- In 1933 Kharasch and Mayo observed that when HBr is added to an unsymmetrical double bond in the presence of organic peroxide, the reaction takes place opposite to the Markovnikov rule.





Noted:- peroxide effect is applicable only to HBr and not to HF, HCl and HI. Addition of HF, HCl and HI takes place according to Markovnikov's rule even in the presence of peroxide.

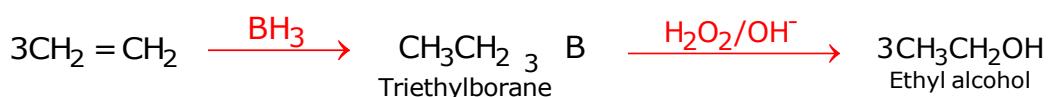
4. Addition of water (Hydration):- Acid catalyzed addition of water



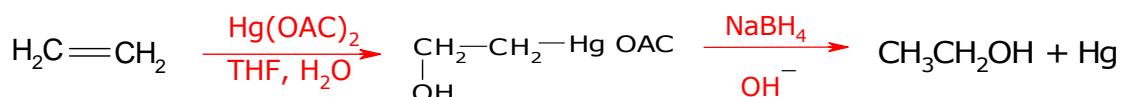
② Oxidation:-

① Combustion:- $\text{CO}_2 + \text{H}_2\text{O}$

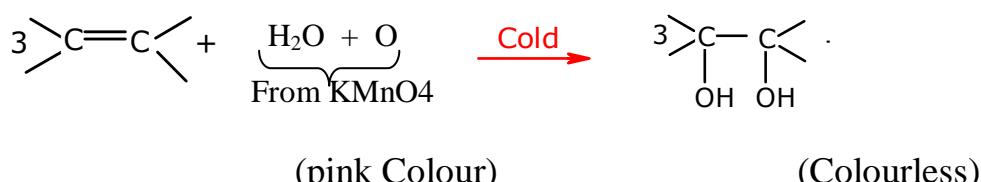
② Hydroboration–oxidation:- Alkanes react with diborane to form trialkyl boranes which on oxidation with alkaline $\text{H}_2\text{O}_2/\text{OH}^-$ give alcohols.



③ Oxymercuration–demercuration:-



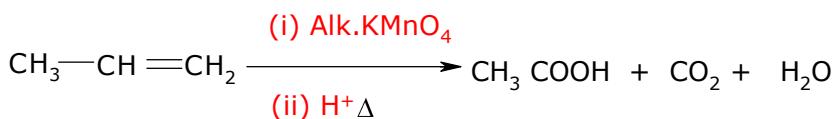
④ Oxidation with potassium permanganate:-



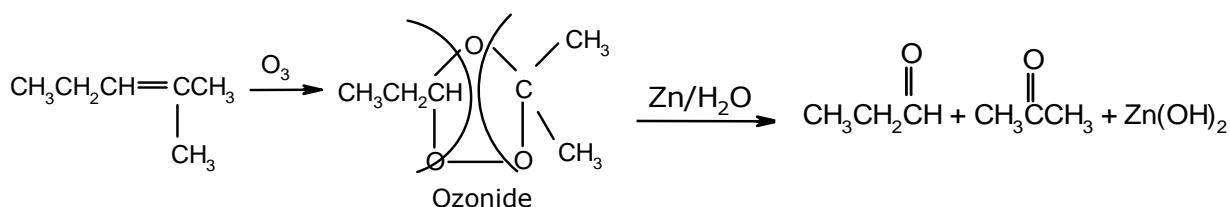
➤ This reaction is also called *Hydroxylation*

➤ *Cis product I.e. cis-diol* is obtained.

Noted:- The alkaline potassium permanganate solution is known as Baeyer's reagent. It has bright pink colour. It oxidizes alkenes to glycols which is colourless. This reaction is used as a test for the presence of double bond in a molecule. This is also known as Baeyer test.



☺ Oxidation with Ozone:- Ozonolysis – give carbonyls compounds



Noted:- Bromine water test and Baeyer's test are used to detect the presence of double bond while ozonolysis is used to detect the position of double bond.

Alkynes

❖ Unsaturated hydrocarbon which have triple bond.

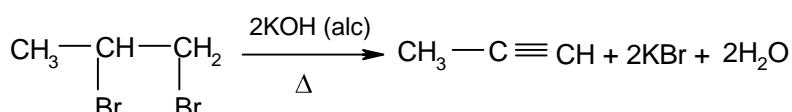
❖ General molecular formula $\text{C}_n\text{H}_{2n-2}$

❖ sp hybridization

❖ Shows chain, positional and functional isomerism

❖ Preparation:-

From vicinal dihalides: - dehalogenation



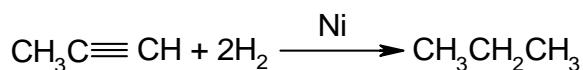
By the action of water on calcium carbide:-



❖ Chemical Properties:-

① Addition Reaction:- Alkyne show electrophilic addition reaction.

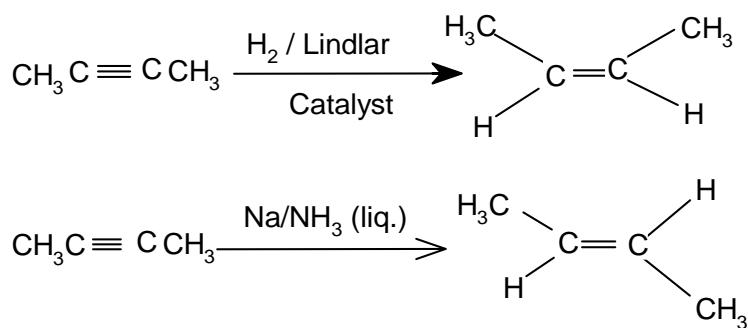
② Addition of Hydrogen:- Hydrogenation.



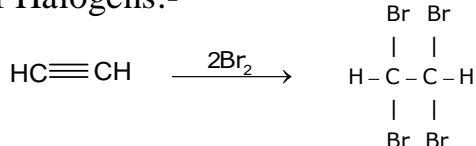
Propyne

Noted:- It may be noted that the hydrogenation can be controlled at the alkene stage only. This is possible by using a *Lindlar's catalysts* or *sodium in liquid NH₃* at 200k temp..

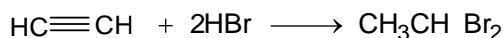
Noted:- It may be again noted that the catalytic reduction of alkynes in the presence of Lindlar's catalyst gives cis-alkenes while in the presence of sodium in liquid NH₃ (Birch reduction) gives trans-alkenes.



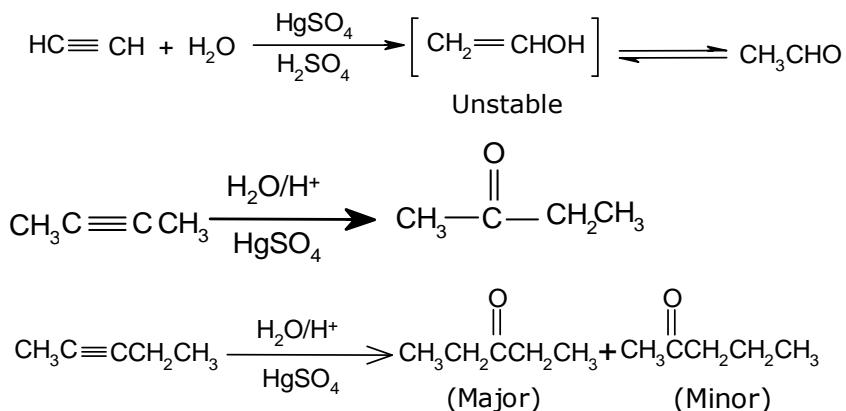
② Addition of Halogens:-



③ Addition of hydrogen halides:-

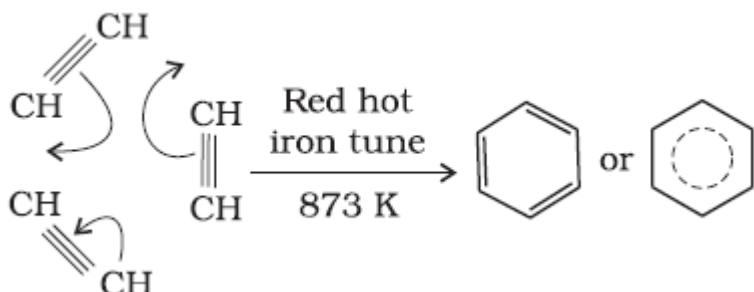


④ Addition of water (Hydration):- Acid catalyzed addition of water

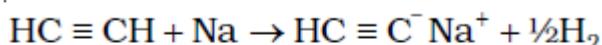


5. Polymerisation-

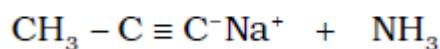
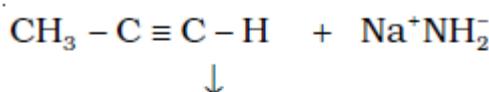
- a. ***Linear polymerisation:*** of ethyne gives polyacetylene or polyethyne which is a high molecular weight polyene containing repeating units of (CH = CH – CH = CH) and can be represented as —(CH = CH – CH = CH)_n—
- b. Cyclic polymerization- results in the formation of aromatic compound.



Acidity of Alkynes- Terminal alkynes are acidic in nature.



Monosodium
ethynide



Sodium propynide

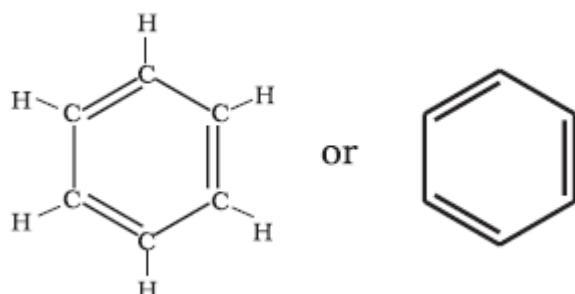
Alkanes, alkenes and alkynes follow the following trend in their acidic behaviour :

- i) $\text{HC} \equiv \text{CH} > \text{H}_2\text{C} = \text{CH}_2 > \text{CH}_3 - \text{CH}_3$
- ii) $\text{HC} \equiv \text{CH} > \text{CH}_3 - \text{C} \equiv \text{CH} > \text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$

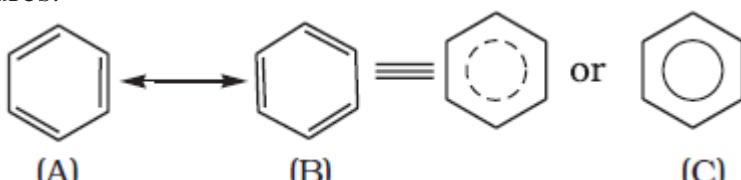
AROMATIC HYDROCARBON

Aromatic compounds containing benzene ring are known as **benzenoids** and those not containing a benzene ring are known as **non-benzenoids**.

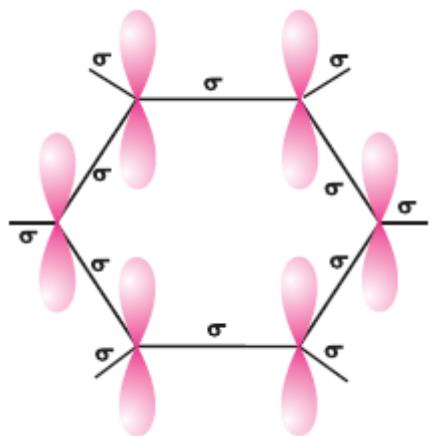
Structure of Benzene- Kekulé structure



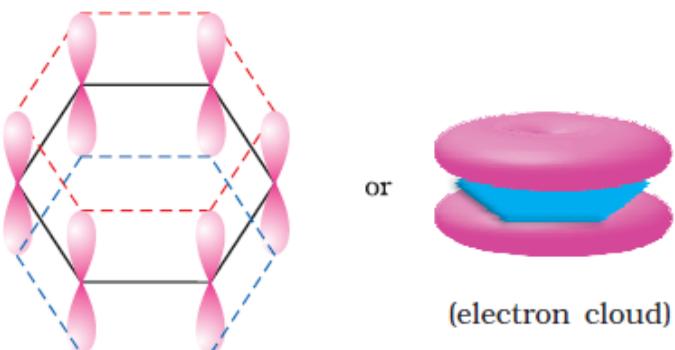
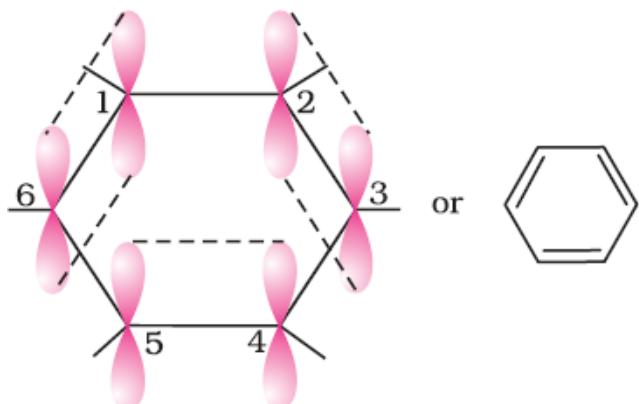
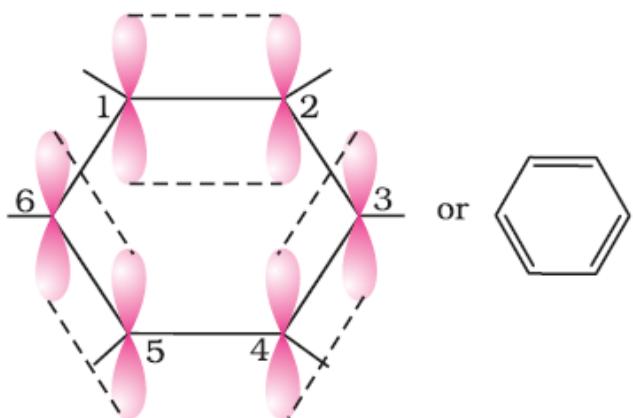
Resonance and stability of benzene- Benzene is a hybrid of various resonating structures.



The orbital overlapping picture benzene- All the six carbon atoms in benzene are sp^2 hybridized and these hybrid orbitals form sigma bonds.



The unhybridised p orbital of carbon atoms are close enough to form a π bond by lateral overlap.



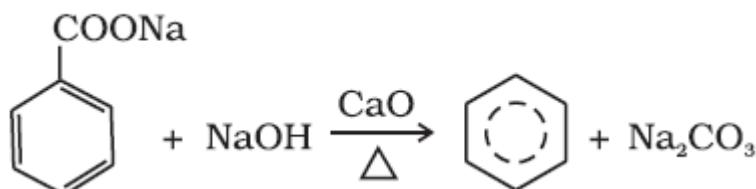
The six π electrons are thus delocalised and can move freely about the six carbon nuclei. The delocalised π electron cloud is attracted more strongly by the nuclei of the carbon atoms than the electron cloud localized between two carbon atoms. Therefore, presence of delocalised π electrons in benzene makes it more stable .

Aromaticity:- The compounds that follow the following features are to be considered aromatic.

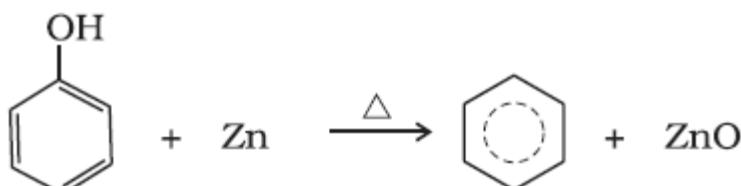
- (i) Planarity
- (ii) Complete delocalisation of the π electrons in the ring
- (iii) Presence of $(4n + 2)$ π electrons in the ring where n is an integer ($n = 0, 1, 2, \dots$). This is often referred to as **Hückel Rule**.

Preparation of Benzene:

- (i) Cyclic polymerisation of ethyne:
- (ii) Decarboxylation of aromatic acids:



(iii) *Reduction of phenol:* Phenol is reduced to benzene by passing its vapours over heated zinc dust



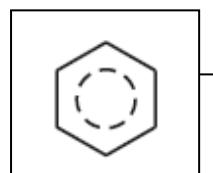
Physical properties:

1. Aromatic hydrocarbons are non-polar molecules and are usually colourless liquids or solids with a characteristic aroma.
2. Aromatic hydrocarbons are immiscible with water but are readily miscible with organic solvents.
3. They burn with sooty flame.

Chemical properties

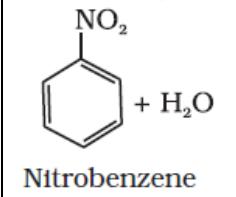
Arenes are characterised by electrophilic substitution reactions proceed via the following three steps:

- (a) Generation of the electrophile
- (b) Formation of carbocation intermediate
- (c) Removal of proton from the carbocation intermediate



Nitration

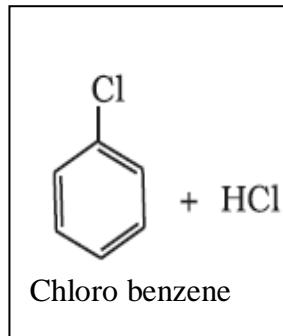
Conc. HNO_3 +Conc. H_2SO_4



Halogenation

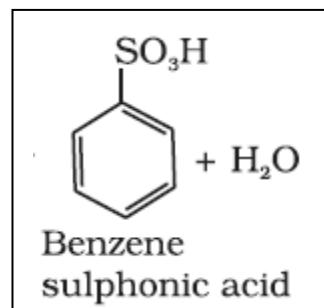
$+\text{Cl}_2$

Anhyd. AlCl_3



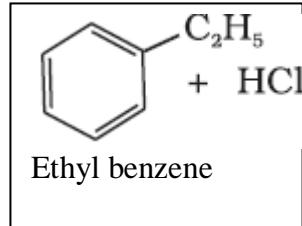
Sulphonation

Fuming sulphuric acid
 $\text{H}_2\text{SO}_4(\text{SO}_3)$



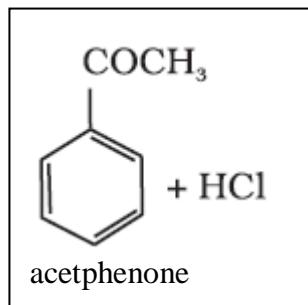
Friedel-Crafts alkylation

$+\text{C}_2\text{H}_5\text{Cl}$
 Anhyd. AlCl_3

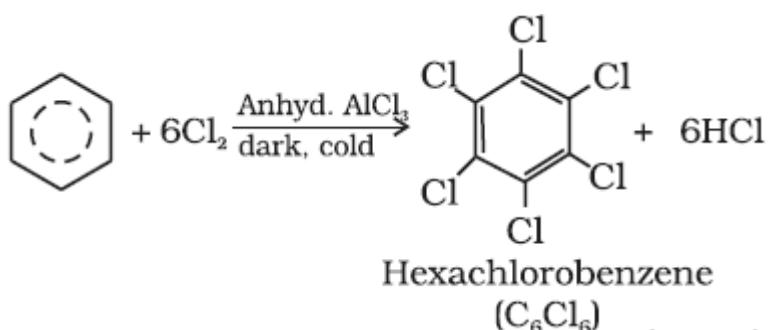


Friedel-Crafts acylation

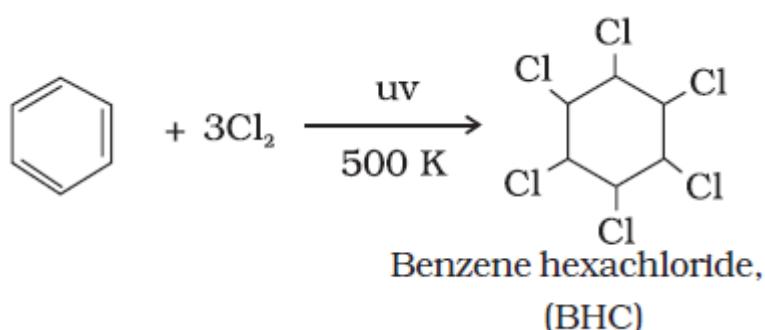
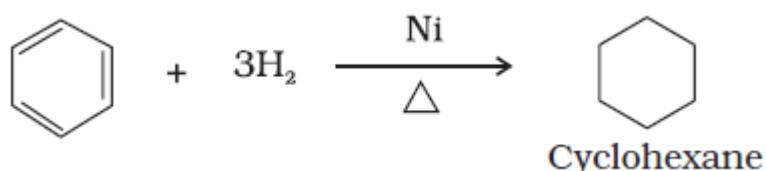
$+\text{CH}_3\text{COCl}$
 Anhyd. AlCl_3



benzene on treatment with excess of chlorine in the presence of anhydrous AlCl_3 in dark yields hexachlorobenzene (C_6Cl_6)

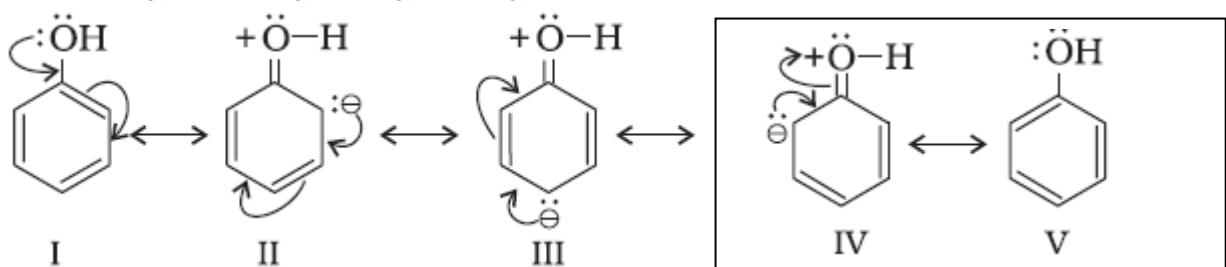


Addition reactions of benzene-

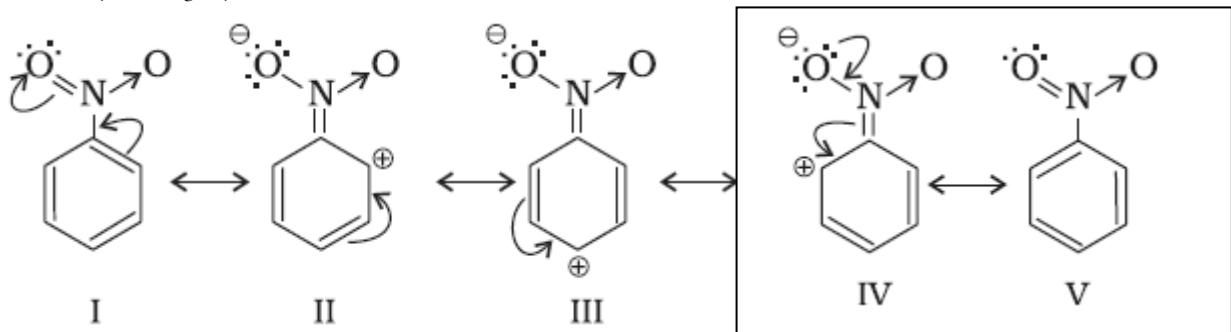


Directive influence of a functional group in monosubstituted benzene:-

1. Ortho and para directing groups and activating- -OH, -NH₂, -NHR, -NHCOCH₃, -OCH₃, -CH₃, -C₂H₅, etc.



2. Meta directing group and deactivating: -NO₂, -CN, -CHO, -COR, -COOH, -COOR, -SO₃H, etc.



3. Ortho and para directing groups and deactivating- Halogens because of their strong – I effect, overall electron density on benzene ring decreases. However,

due to resonance the electron density on *o*- and *p*- positions is greater than that at the *m*-position. Hence, they are also *o*- and *p*- directing groups.

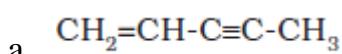
CARCINOGENICITY AND TOXICITY-Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer producing (carcinogenic) property.

ONE MARK QUESTIONS

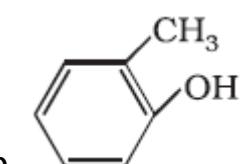
1. What are hydrocarbons?
Ans. Compounds of hydrogen and carbon.
2. What is the general formula of alkanes?
Ans. C_nH_{2n+2}
3. Write the general formula of alkenes.
Ans. C_nH_{2n}
4. What is the general formula of alkynes?
Ans. C_nH_{2n-2}
5. Give the IUPAC name of lowest molecular weight alkane that contains a quaternary carbon.
Ans. 2,2dimethylpropane.
6. Arrange the following in the increasing order of C-C bond length-
 C_2H_6 C_2H_4 C_2H_2
Ans. $C_2H_2 < C_2H_4 < C_2H_6$
7. Out of ethylene and acetylene which is more acidic and why?
Ans. Acetylene, due to greater electronegativity of the sp hybrid carbon.
8. Name two reagents which can be used to distinguish between ethene and ethyne.
Ans. Tollen's reagent and ammonical $CuCl$ solution.
9. Arrange the following in order of decreasing reactivity towards alkanes.
 HCl , HBr , HI , HF
Ans. $HI > HBr > HCl > HF$
10. How will you detect the presence of unsaturation in an organic compound?
Ans. Generally Unsaturated organic compound decolourise Bayer's reagent and Bromine water.
11. What is Grignard reagent?
Ans. Alkyl magnesium halides

TWO MARKS QUESTIONS

1. Write the IUPAC names of the following-

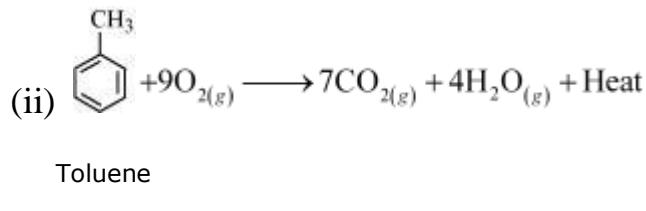
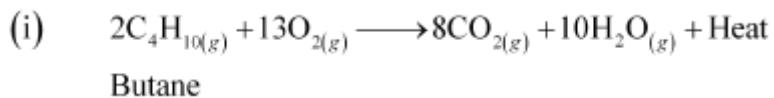


Ans. a .Pent-en-3-yne



b. 2-methylphenol

2. Write chemical equations for combustion reaction of (i) Butane (ii) Toluene
 Ans.



3. What are the necessary conditions for any system to be aromatic?

Ans. A compound is said to be aromatic if it satisfies the following three conditions: (i) It should have a planar structure.

(ii) The π -electrons of the compound are completely delocalized in the ring.

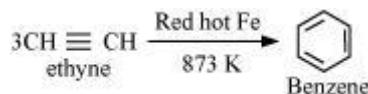
(iii) The total number of π -electrons present in the ring should be equal to $(4n + 2)$, where $n = 0, 1, 2 \dots$ etc. This is known as Huckel's rule.

4. What effect does branching of an alkane chain has on its boiling point?

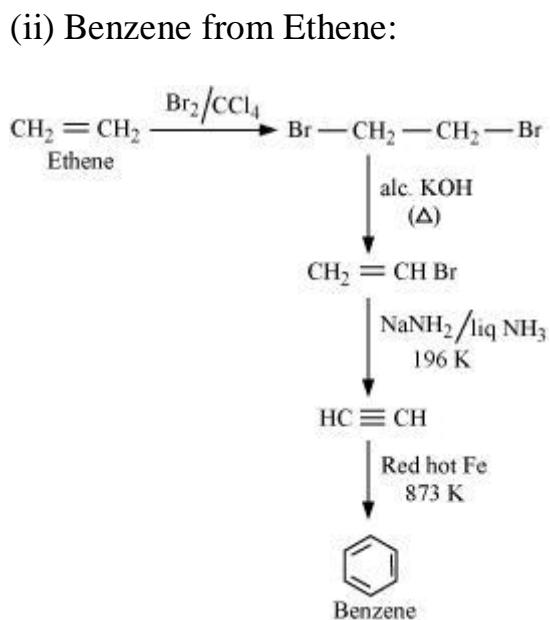
Ans. As branching increases, the surface area of the molecule decreases which results in a small area of contact. As a result, the Van der Waals force also decreases which can be overcome at a relatively lower temperature. Hence, the boiling point of an alkane chain decreases with an increase in branching.

5. How would you convert the following compounds into benzene?

(i) Ethyne (ii) Ethene

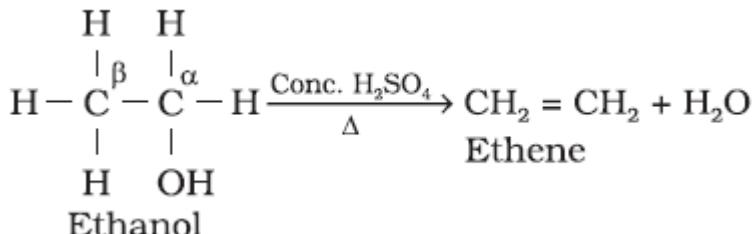


Ans. (i) Benzene from Ethyne:



6. Suggest the name of Lewis acids other than anhydrous aluminium chloride which can be used during ethylation of benzene.
 Ans. anhydrous FeCl_3 , SnCl_4 , BF_3 etc.
7. Write the name of all the possible isomers of $\text{C}_2\text{H}_2\text{Cl}_2$ and indicate which of them is non-polar.
 Ans.(i) cis-1,2-dichloroethene (ii) trans-1,2-dichloroethene (iii) 1,1-dichloroethene. trans-1,2-dichloroethene is non-polar.
8. Although benzene is highly unsaturated, it does not undergo addition reactions, why?
 Ans. Because of extra stability due to delocalization of π -electrons.
9. What are alkanes? Why are they called paraffins?
 Ans. Those hydrocarbons which contain single bond between carbon- carbon are called alkanes. They are called paraffins because they are very less reactive (Latin- Parum= little, affins = affinity)
10. How can ethene be prepared from (i) ethanol (ii) ethyl bromide?

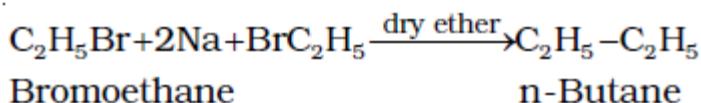
Ans. (i) Ethene from ethanol- by acidic dehydration of alcohols



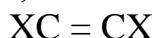
(ii) Ethene from ethyl bromide- by dehydrohalogenation of ethyl bromide
 $\text{CH}_3\text{CH}_2\text{Br} + \text{KOH} \text{ (alc)} \rightarrow \text{H}_2\text{C}=\text{CH}_2 + \text{KBr} + \text{H}_2\text{O}$

THREE MARKS QUESTIONS

1. What is Wurtz reaction? How can it be used to prepare butane?
 Ans- When alkyl halides is treated with metallic Na in presence of dry ether, alkanes are formed. This reaction is called Wurtz reaction.
 Butane is prepared by the reaction of bromoethane with metallic Na in presence of dry ether

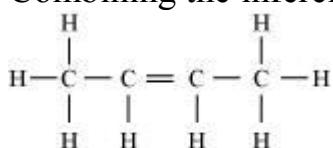


2. An alkene 'A' contains three C – C, eight C – H σ bonds and one C – C π bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Deduce IUPAC name of 'A'.
 Ans.. The formation of two moles of an aldehyde indicates the presence of identical structural units on both sides of the double bond containing carbon atoms. Hence, the structure of 'A' can be represented as:



There are eight C–H σ bonds. Hence, there are 8 hydrogen atoms in 'A'. Also, there are three C–C bonds. Hence, there are four carbon atoms present in the structure of 'A'.

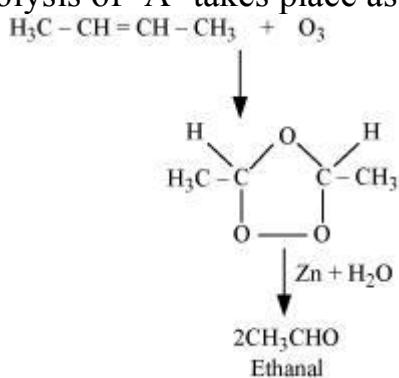
Combining the inferences, the structure of 'A' can be represented as:



(A)

the IUPAC name of 'A' is But-2-ene.

Ozonolysis of 'A' takes place as:



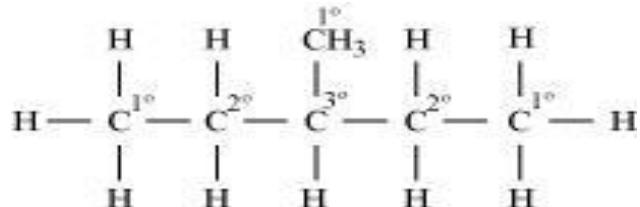
The final product is ethanal with molecular mass

$$= \left[(2 \times 12) + (4 \times 1) + (1 \times 16) \right] = 44 \text{ u}$$

3. In the alkane $\text{H}_3\text{C} - \text{CH}_2 - \text{C}(\text{CH}_3)_2 - \text{CH}_2 - \text{CH}(\text{CH}_3)_2$, identify $1^\circ, 2^\circ, 3^\circ$ carbon atoms and give the number of H atoms bonded to each one of these.

Ans

Ans.



The given structure has five 1° carbon atoms and fifteen hydrogen atoms attached to it.

The given structure has two 2° carbon atoms and four hydrogen atoms attached to it.

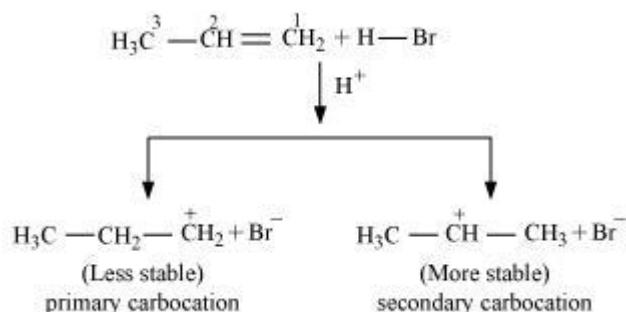
The given structure has one 3° carbon atom and only one hydrogen atom is attached to it.

FIVE MARKS QUESTIONS

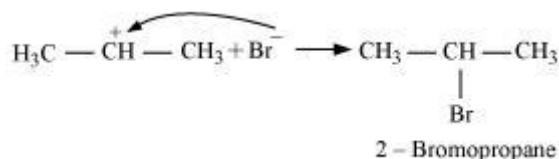
4. Addition of HBr to propene yields 2-bromopropane, while in the presence of benzoyl peroxide, the same reaction yields 1-bromopropane. Explain and give mechanism

Ans. Addition of HBr to propene is an example of an electrophilic substitution reaction.

Hydrogen bromide provides an electrophile, H^+ . This electrophile attacks the double bond to form 1° and 2° carbocations as shown:

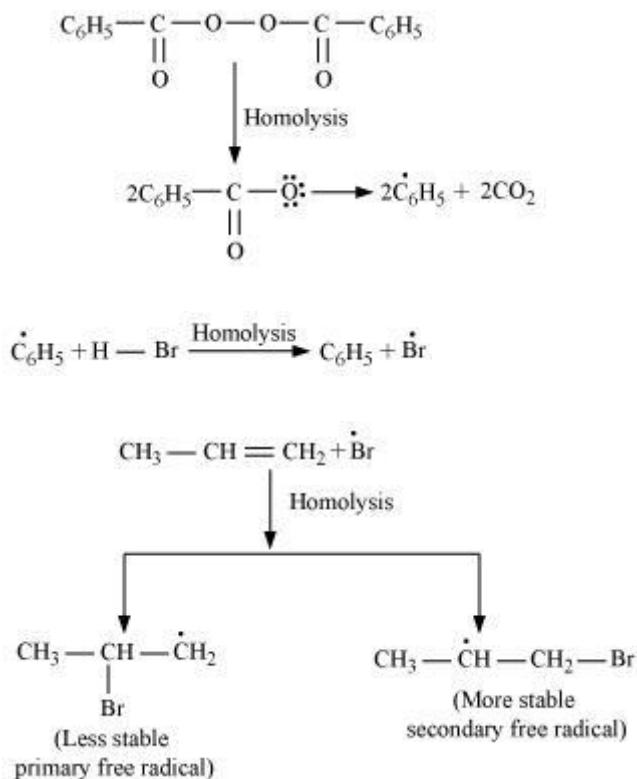


Secondary carbocations are more stable than primary carbocations. Hence, the former predominates since it will form at a faster rate. Thus, in the next step, Br^- attacks the carbocation to form 2 – bromopropane as the major product.

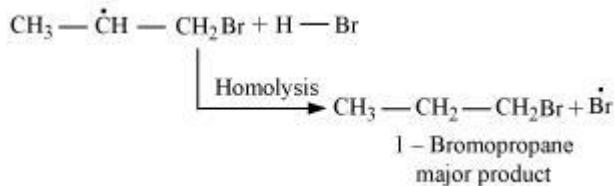


This reaction follows Markovnikov's rule

In the presence of benzoyl peroxide, an addition reaction takes place anti to Markovnikov's rule. The reaction follows a free radical chain mechanism as:



Secondary free radicals are more stable than primary radicals. Hence, the former predominates since it forms at a faster rate. Thus, 1 – bromopropane is obtained as the major product.



HOTS QUESTIONS

1. How will you demonstrate that double bonds of benzene are somewhat different from that of olefins?

Ans. The double bonds of olefins decolourize bromine water and discharge the pink colour of Bayer's reagent while those of benzene not

2. How will you separate propene from propyne?

Ans. By passing the mixture through ammonical silver nitrate solution when propyne reacts while propene passes over.

3. Write the structure of the alkene which on reductive ozonolysis gives butanone and ethanol,

Ans. $-\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_3$

CHAPTER 14

ENVIRONMENTAL CHEMISTRY

- Environmental chemistry deals with the study of the origin, transport, reactions, effects, fates of chemical species in the environment.
 - **ENVIRONMENTAL POLLUTION:**-Environmental pollution is the effect of undesirable changes in our surroundings that have harmful effects on plants, animals and human beings. A substance which causes pollution is called a pollutant. They can be solid, liquid or in the gaseous state.
 - **ATMOSPHERIC POLLUTION:**-The atmosphere that surrounds the earth is not of the same thickness at different heights. Atmospheric pollution is generally studied as tropospheric and stratospheric pollution. The ozone layer prevents about 99.5% of the sun's UV rays.
 - **TROPOSPHERIC POLLUTION:**-Tropospheric pollution occurs due to the presence of undesirable solid or gaseous particles in the air. The following are the major gaseous and particulate pollutants present in the troposphere;
 - Gaseous air pollutants: These are oxides of sulphur, nitrogen and carbon, hydrogen sulphide, hydrocarbons, ozone and other oxidants.
 - Particulate pollutants; these are dust, mist, fumes, smoke, smog etc
 - **GLOBAL WARMING AND GREENHOUSE EFFECT:**-About 75% of the solar energy reaching the earth is absorbed by the earth's surface, which increases its temperature. The rest of the heat radiates back to the atmosphere. Some of the heat is trapped by the gases such as carbon dioxide, methane, ozone, CFCS and Water vapour. They add to the heating of the atmosphere causing Global warming
- In a greenhouse, visible light passes through the transparent glass and heats up the soil and the plants. The warm soil and plants emit infrared rays, it partly reflects and partly absorbs these radiations, this mechanism keeps the energy of the sun trapped in the greenhouse.
- **ACID RAIN:** When the pH of the rain water drops below 5.6, it is called acid rain. Acid rain is harmful for agriculture, trees and plants as it dissolves and washes away nutrients needed for their growth. It causes respiratory ailments

in human beings and animals. When acid rain falls and flows as ground water to reach rivers, lakes etc. it affects plants and animal life in aquatic ecosystem

- **SMOG:**The word smog is derived from smoke and fog. There are two types of smog:classical and photochemical smog. Classical smog occurs in cool humid climate. It is a mixture of smoke, fog and sulphur dioxide. It is also called reducing smog. Whereas photochemical smog occurs in warm and dry sunny climate. It has high concentration of oxidizing agents and therefore ,it is also called as oxidizing smog
- **OZONE HOLE:**Depletion of ozone layer is known as ozone hole.
- **EFFECTS OF DEPLETION OF THE OZONE LAYER:** With the depletion of ozone layer, more UV radiation filters into troposphere. UV radiations lead to ageing of skin, cataract, sunburn, skin cancer, killing of many phytoplanktons, damage to fish productivity etc
- **WATER POLLUTION:-**contamination of water by foreign substances which make it harmful for health of animals or plants or aquatic life and make it unfit for domestic, industrial and agriculture use.
- **SOURCES/ CAUSES OF WATER POLLUTION-**
 - Sewage and domestic wastes
 - Industrial effluents
 - Agriculture effluents
 - Siltation-mixing of soil or rock into water
 - Thermal pollutants
 - Radioactive discharge
- **EUTROPHICATION:**The process in which nutrientenriched water bodies support a dense plantpopulation, which kills animal life by deprivingit of oxygen and results in subsequent loss ofbiodiversity is known asEutrophication
- **BOD:** The amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water, is called Biochemical Oxygen Demand (BOD)
- **SOIL POLLUTION:**Insecticides, pesticides and herbicides cause soil pollution.

GREEN CHEMISTRY: Green chemistry is a way of thinking and is about utilizing the existing knowledge and principles of chemistry and other sciences to reduce the adverse impact on environment. Green chemistry is a production process that would bring out minimum pollution or deterioration to the environment.. Utilization of existing knowledge base for reducing the chemical hazards along with the development of activities is the foundation of green chemistry.

ONE MARK QUESTION

1. What is the name of the compound formed when CO combines with blood?
Ans:-Carboxyhaemoglobin.
2. Which zone is known as ozonosphere?
Ans:-Stratosphere.
3. Which main gas is responsible for damage in ozone layer?
Ans:-NO and CFCs(freons).
4. What is the nature of classical smog?
Ans:-Reducing
5. Name the acids which are responsible for acid rain?
Ans:- H_2SO_4 , HNO_3 and HCl .
6. List out the gasses which are considered as major source of air pollution?
Ans:-Carbon monoxide(CO), sulphur dioxide(SO_2) and oxides of nitrogen(NO_2).
7. What is PAN stands for?
Ans:-It is peroxyacetyl nitrate.
8. Give the examples of insecticides?
Ans:-DDT, BHC.
9. Which gas is mainly responsible for BHOPAL gas tragedy?
Ans:-Methyl isocyanate.
10. What should be the tolerable limit of F^- ions in drinking water?
Ans:-1 ppm or 1mg dm^{-3} .

TWO MARKS QUESTION

1. What is ‘acid rain’? How is it harmful to the environment?
Ans:- Acid rain is the rain water mixed with small amount of sulphuric acid, nitric acid along with hydrochloric acid which are formed from the oxides of sulphur and nitrogen present in air as pollutants. It has a pH of 4-5.
Harmful effects of acid rain:-
It is toxic to vegetation and aquatic life.
It damages buildings and statues

2. What do you mean by Green house effect ?What is the role of CO₂ in the greenhouse effect.

Ans:-It is the phenomenon in which earth's atmosphere traps the heat from the sun and prevents it from escaping in outer space. Gases such as CO₂,methane,ozone,CFCs are believed to be responsible for this effect.

Heat from the sun after being absorbed by the earth absorbed by CO₂ and then radiated back to the earth.Thus making the environment of the earth warm.

3. Which gases are responsible for greenhouse effect?List some of them.

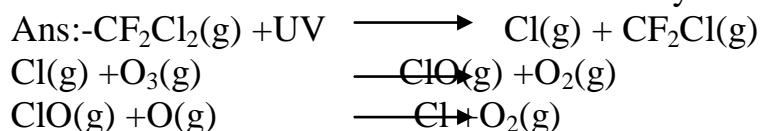
Ans:-CO₂ is mainly responsible for greenhouse effect.Other greenhouse gases are methane nitrous oxide, water vapours.

4. What is smog?How is classical smog different from photochemical smog?

Ans:-The word smog is a combination of smoke and fog.It is a type of air pollution that occurs in many cities throughout the world.Classical smog occurs in cool humid climate.It is also called reducing smog.

Whereas photochemical smog occurs in warm and dry sunny climate. It has high concentration of oxidizing agents and therefore ,it is also called as oxidizing smog.

5. What are the reactions involved for ozone layer depletion in the stratosphere?



6. What is the full form of BOD and COD?

Ans:-BOD stands for Biochemical Oxygen Demand whereas COD stands for Chemical Oxygen Demand.

7. What are viable and non-viable particulates?

Ans:-Viable particulates:-They are minute living organisms that are dispersed in the atmosphere including bacteria,fungi,moulds,algae etc.

Non-viable particulates:-They are formed by the breakdown of larger materials or by the condensation of minute particles and droplets.

8. What is B.H.C?Give its IUPAC name?

Ans:-B.H.C is BENZENE HEXACHLORIDE Its IUPAC name is 1,2,3,4,5,6-hexa chlorocyclohexane.

9. What is meant by PCBs?

Ans:-PCBs are polychlorinated biphenyls.They are contaminants of water. They are used as fluids in transformers and capacitors.

- 10.What is the compound formed when CO combines with blood?

Ans:-When CO combines with blood, the following reaction occurs forming carboxyhaemoglobin:-



THREE MARKS QUESTION

1. What do you understand by- (i) Mist (ii) Smoke (iii) Fumes
Ans(i) Mists:-Mists are produced by particles of spray liquids and the condensation of vapours in air.
(ii)Smoke:- They are very small soot particles produced by burning of organic matter.
(iii)Fumes:- These are condensed vapours;fumes of metals are well known particulates of this type.
2. Define the term pesticides? What are three categories of pesticides?
Ans:-Pesticides are substances which are used to kill or block the reproductive process of unwanted organisms.
The three main categories of pesticides are:-
(i)Insecticides:-These are used to control insects and curb diseasesand protect crops.
(ii)Herbicides:-These are used to kill weeds .Example- sodium chlorate (NaClO_3), sodium arsinite(Na_3AsO_3)
(iii)Fungicides:- These are used to check the growth of fungi. Example-methyl, mercury.
3. What do you mean by ozone hole? What are its consequences?
Ans:-Depletion of ozone hole creates some sort of holes in the blanket of ozone which surround as. This is known as ozone hole.
(i)With the depletion of the ozone layer UV radiation filters into the troposphere which leads to aging of skin,cataract,sunburn etc.
(ii)By killing many of the phytoplanktons it can damage the fish productivity.
4. What are harmful effects of photochemical smog and how can they becontrolled?
Ans:- (i)Photochemical smog causes eye irritation.
(ii)It damages plants (the leaves develop a metallic sheen)
(iii)Rubber on exposure to photochemical smog loses its elasticity and becomes inflexible and brittle.
Usually catalytic converters are used in the automobiles, which prevent the release of nitrogen oxide and hydrocarbons to the atmosphere. Certain plants e.g., Pinus, Juniperus, Quercus, Pyrus and Vitis can metabolise nitrogen oxide and therefore, their plantation could help in this matter.
5. Give three examples in which green chemistry has been applied.
Ans:-
(i) In dry cleaning ,use of liquefied CO_2 in place of tetrachloroethene($\text{Cl}_2\text{C}=\text{CCl}_2$)
(ii)In bleaching of paper using H_2O_2 in place of chlorine.
(iii)In the manufacture of chemicals like ethanal using environment-friendly chemicals and conditions.

ENJOY CHEMISTRY

1. SOME BASIC CONCEPTS OF CHEMISTRY

Some Important Points and Terms of the Chapter

1. Anything which has mass and occupies space is called **matter**.
2. Matters exist in three physical states viz. solid, liquid and gas.
3. In solids, these particles are held very close to each other in an orderly fashion and there is not much freedom of movement. In liquids, the particles are close to each other but they can move around. However, in gases, the particles are far apart as compared to those present in solid or liquid states and their movement is easy and fast.
4. Solids have definite volume and definite shape.
5. Liquids have definite volume but not the definite shape. They take the shape of the container in which they are placed.
6. Gases have neither definite volume nor definite shape. They completely occupy the container in which they are placed.
7. A mixture contains two or more substances present in it (in any ratio) which are called its components.
8. A **mixture** may be homogeneous or heterogeneous.
9. In a **homogeneous mixture**, the components completely mix with each other and its composition is uniform throughout. Sugar solution and air are thus, the examples of homogeneous mixtures.
10. In **heterogeneous mixtures**, the composition is not uniform throughout and sometimes the different components can be observed. For example, the mixtures of salt and sugar, grains and pulses along with some dirt (often stone) pieces, are heterogeneous mixtures..
11. The components of a mixture can be separated by using physical methods such as simple hand picking, filtration, crystallization, distillation etc.
12. **Pure substances** have characteristics different from the mixtures. They have fixed composition, Copper, silver, gold, water, glucose are some examples of pure substances.

Glucose contains carbon, hydrogen and oxygen in a fixed ratio and thus, like all other pure substances has a fixed composition. Also, the constituents of pure substances cannot be separated by simple physical methods.

13. An **element** consists of only one type of particles. These particles may be atoms or molecules. Sodium, copper, silver, hydrogen, oxygen etc. are some examples of elements. They all contain atoms of one type. However, the atoms of different elements are different in nature. Some elements such as sodium or copper, contain single atoms held together as their constituent particles whereas in some others, two or more atoms combine to give molecules of the element. Thus, hydrogen, nitrogen and oxygen gases consist of molecules in which two atoms combine to give their respective molecules.
14. When two or more atoms of different elements combine, the molecule of a **compound** is obtained. The examples of some compounds are water, ammonia, carbon dioxide, sugar etc. the atoms of different elements are present in a compound in a fixed and definite ratio and this ratio is characteristic of a particular compound.
15. The **SI system**(Système International d'Unités –abbreviated as SI)) has seven base units and they are listed in Table 1.1

Table 1.1 Base Physical Quantities and their Units

| Base Physical Quantity | Symbol for Quantity | Name of SI Unit | Symbol for SI Unit |
|---------------------------|----------------------|-----------------|--------------------|
| Length | <i>l</i> | metre | <i>m</i> |
| Mass | <i>m</i> | kilogram | <i>kg</i> |
| Time | <i>t</i> | second | <i>s</i> |
| Electric current | <i>I</i> | ampere | <i>A</i> |
| Thermodynamic temperature | <i>T</i> | kelvin | <i>K</i> |
| Amount of substance | <i>n</i> | mole | <i>mol</i> |
| Luminous Intensity | <i>I_v</i> | candela | <i>cd</i> |

16. **Mass** of a substance is the amount of matter present in it while **weight** is the force exerted by gravity on an object. The mass of a substance is constant whereas its weight may vary from one place to another due to change in gravity.
17. **Volume** has the units of (length)³. So in SI system, volume has units of m³. A common unit, litre (L) which is not an SI unit, is used for measurement of volume of liquids. 1 L = 1000 mL , 1000 cm³ = 1 dm³

18. **Density** of a substance is its amount of mass per unit volume SI units of density kg m^{-3}

This unit is quite large and a chemist often expresses density in g cm^{-3} .

19. There are three common scales to measure temperature — **$^{\circ}\text{C}$ (degree celsius)**, **$^{\circ}\text{F}$ (degree Fahrenheit)** and **K (Kelvin)**. Here, K is the SI unit.

20. The **Kelvin scale is related to Celsius scale** as follows : $\text{K} = ^{\circ}\text{C} + 273.15$

21. The **$^{\circ}\text{F}$ scale is related to Celsius scale** as follows

$$^{\circ}\text{F} = \frac{9}{5} (^{\circ}\text{C}) + 32$$

22. In **scientific notation (exponential Notation)** any number can be represented in the form $N \times 10^n$ where n is an exponent having positive or negative values and N can vary between 1 to 10. Thus, we can write 232.508 as 2.32508×10^2 in scientific notation. Note that while writing it, the decimal had to be moved to the *left* by two places and same is the exponent (2) of 10 in the scientific notation. Similarly, 0.00016 can be written as 1.6×10^{-4} . Here the decimal has to be moved four places to the *right* and (- 4) is the exponent in the scientific notation.

23. **Significant figures** are meaningful digits which are known with certainty. The uncertainty is indicated by writing the certain digits and the last uncertain digit. Thus, if we write a result as 11.2 mL, we say the 11 is certain and 2 is uncertain and the uncertainty would be ± 1 in the last digit. Unless otherwise stated, an uncertainty of +1 in the last digit is always understood.

24. There are certain **rules for determining the number of significant figures**. These are stated below:

- a) All non-zero digits are significant. For example in 285 cm, there are three significant figures and in 0.25 mL, there are two significant figures.
- b) Zeros preceding to first non-zero digit are not significant. Such zero indicates the position of decimal point. Thus, 0.03 has one significant figure and 0.0052 has two significant figures.
- c) Zeros between two non-zero digits are significant. Thus, 2.005 has four significant figures.
- d) Zeros at the end or right of a number are significant provided they are on the right side of the decimal point. For example, 0.200 g has three significant figures. But, if otherwise, the terminal zeros are not significant if there is no decimal point. For example, 100 has only one significant figure, but 100. has three significant figures and 100.0 has four significant

figures. Such numbers are better represented in scientific notation. We can express the number 100 as 1×10^2 for one significant figure, 1.0×10^2 for two significant figures and 1.00×10^2 for three significant figures.

- e) Counting numbers of objects, for example, 2 balls or 20 eggs, have infinite significant figures as these are exact numbers and can be represented by writing infinite number of zeros after placing a decimal i.e., $2 = 2.000000$ or $20 = 20.000000$
- f) In numbers written in scientific notation, all digits are significant e.g., 4.01×10^2 has three significant figures, and 8.256×10^{-3} has four significant figures.

25. **Law of Conservation of Mass** states that matter can neither be created nor destroyed.

26. **Law of Definite Proportions** states that a given compound always contains exactly the same proportion of elements by weight.

27. **Law of Multiple Proportions** states that if two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in the ratio of small whole numbers.

28. **Gay Lussac's Law of Gaseous Volumes:** This law was given by Gay Lussac in 1808. He observed that when gases combine or are produced in a chemical reaction they do so in a simple ratio by volume provided all gases are at same temperature and pressure.

29. In 1811, Avogadro proposed that equal volumes of gases at the same temperature and pressure should contain equal number of molecules.

30. In 1808, Dalton published '**A New System of Chemical Philosophy**' in which he proposed the following :

- a) Matter consists of indivisible atoms.
- b) All the atoms of a given element have identical properties including identical mass.
Atoms of different elements differ in mass.
- c) Compounds are formed when atoms of different elements combine in a fixed ratio.
- d) Chemical reactions involve reorganization of atoms. These are neither created nor destroyed in a chemical reaction.
- e) Dalton's theory could explain the laws of chemical combination.

31. One **atomic mass unit** is defined as a mass exactly equal to one twelfth the mass of one carbon - 12 atom.

32. **Molecular mass** is the sum of atomic masses of the elements present in a molecule. It is obtained by multiplying the atomic mass of each element by the number of its atoms and adding them together.
33. The **mole** is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12; its symbol is “mol.” When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles. This number of entities in 1 mol is so important that it is given a separate name and symbol. It is known as ‘**Avogadro constant**’, denoted by N_A in honor of Amedeo Avogadro.
34. An **empirical formula** represents the simplest whole number ratio of various atoms present in a compound whereas the molecular formula shows the exact number of different types of atoms present in a molecule of a compound.
35. Many a time, the reactions are carried out when the reactants are not present in the amounts as required by a balanced chemical reaction. In such situations, one reactant is in excess over the other. The reactant which is present in the lesser amount gets consumed after sometime and after that no further reaction takes place whatever be the amount of the other reactant present. Hence, the reactant which gets consumed, limits the amount of product formed and is, therefore, called the **limiting reagent**.

36. **Mass per cent** = Mass of solute per 100 g of solution

$$= \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

It is the amount of solute in grams dissolved per 100 g of solution. e.g., 10% solution of sodium chloride means 10 g of solid sodium chloride present in 100 g of solution.

37. **Mole Fraction:** It is ratio of number of moles of a particular component to the total number of moles of all the components.

$$\text{Mole-fraction of solute} = \frac{\text{No.of moles of solute}}{\text{No.of moles of solute} + \text{No.of moles of solvent}}$$

$$x_B = \frac{n_B}{n_A + n_B} = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

$$x_B = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A}} \text{ in case of dilute solution } \therefore \frac{W_B}{M_B} \ll \frac{W_A}{M_A}$$

38. Molality (m). It is defined as number of moles of solute (B) per 1000 g or 1 kg of solvent.

$$\text{Molality (M)} = \frac{\text{No. of moles of solute}}{\text{Kg. of solvent}} = \frac{W_B}{M_A} \times \frac{1000}{W_B \text{ in grams.}}$$

where W_A is mass of solvent.

39. Molarity (M). It is expressed as the number of moles of solute per litre of solution.

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{Litres of solution}} = \frac{W_B}{M_B} \times \frac{1000}{\text{Volume of solution in ml.}}$$

where W_B is mass of solute, M_B is molar mass of solute

Unit-1

SOME BASIC CONCEPTS OF CHEMISTRY

1. Question based on significant numbers, Precision, Accuracy, Scientific Notation, laws of chemical combinations, SI units

1.1 What are the SI unit of mass, length & time?

1.2 Match the following prefixes with their multiples:

| Prefixes | Multiples |
|------------|------------|
| (i) micro | 10^6 |
| (ii) deca | 10^9 |
| (iii) mega | 10^{-6} |
| (iv) giga | 10^{-15} |
| (v) femto | 10 |
| (vi) pico | 10^{-12} |

1.3 (a) What do you mean by significant figures? What are rules for determining the number of significant figures?

(b) Explain the terms: Precision and Accuracy

1.4 Express the following in the scientific notation: (i) 0.0048 (ii) 234,000 (iii) 8008 (iv) 500.0 (v) 6.0012

1.5 How many significant figures are present in the following? (i) 0.0025 (ii) 208 (iii) 5005 (iv) 126,000 (v) 500.0 (vi) 2.0034

1.6 Round up the following upto three significant figures: (i) 34.216 (ii) 10.4107 (iii) 0.04597 (iv) 2808

1.7 The following data are obtained when dinitrogen and dioxygen react together to form different compounds :

| S.No | Mass of dinitrogen | Mass of dioxygen |
|------|--------------------|------------------|
| 1 | 14 g | 16 g |

| | | |
|---|------|------|
| 2 | 14 g | 32 g |
| 3 | 28 g | 32 g |
| 4 | 28 g | 80 g |

(a) Which law of chemical combination is obeyed by the above experimental data? Give its statement.

1.8 Convert the following into basic units: (i) 28.7 pm (ii) 15.15 pm (iii) 25365 mg

1.9 How many significant figures should be present in the answer of the following calculations?

(i)
$$\frac{0.02856 \times 298.15 \times 0.112}{0.5785}$$

 (iii)
$$0.0125 + 0.7864 + 0.0215$$

(ii)
$$5 \times 5.364$$

1.10. State and illustrate the law of constant proportions.

1.11 State and explain the law of multiple proportions.

2. Question based on atomic and molecular masses Atomic Mass Average Atomic Mass,

Molecular Mass, Formula Mass, mole concept and molar Masses, percentage composition,

Empirical Formula for Molecular Formula, Limiting Reagent.

2.1 Calculate the molecular mass of the following: (i) H₂O (ii) CO₂ (iii) CH₄ (iv) C₆H₁₂O₆

2.2 Calculate the mass per cent of different elements present in sodium sulphate (Na₂SO₄).

2.3 Determine the empirical formula of an oxide of iron which has 69.9% iron and 30.1% Dioxygen by mass.

2.4 How much copper can be obtained from 100 g of copper sulphate (CuSO₄)?

2.5 In a reaction A + B₂ → AB₂ Identify the limiting reagent, if any, in the following reaction mixtures.

(i) 300 atoms of A + 200 molecules of B (ii) 2 mol A + 3 mol B

(iii) 100 atoms of A + 100 molecules of B (iv) 5 mol A + 2.5 mol B (v) 2.5 mol A + 5 mol B

2.5 Determine the molecular formula of an oxide of iron in which the mass per cent of iron and oxygen are 69.9 and 30.1 respectively.

2.6 Calculate the atomic mass (average) of chlorine using the following data:

| Isotope | % Natural Abundance | Molar Mass |
|------------------|---------------------|------------|
| ³⁵ Cl | 75.77 | 34.9689 |
| ³⁷ Cl | 24.23 | 36.9659 |

2.7 In three moles of ethane (C₂H₆), calculate the following: (i) Number of moles of carbon atoms. (ii) Number of moles of hydrogen atoms. (iii) Number of molecules of ethane.

2.8 If ten volumes of dihydrogen gas reacts with five volumes of dioxygen gas, how many volumes of water vapour would be produced?

2.9 A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide , 0.690 g of water and no other products. A volume of 10.0 L (measured at STP) of this welding gas is found to weigh 11.6 g. Calculate (i) empirical formula, (ii) molar mass of the gas, and (iii) molecular formula.

2.10 Calculate the amount of water (g) produced by the combustion of 16 g of methane. reaction.

2.11 How many moles of methane are required to produce 22 g CO_2 (g) after combustion?

2.12 A compound contains 4.07 % hydrogen, 24.27 % carbon and 71.65 % chlorine.

Its molar mass is 98.96 g. What are its empirical and molecular formulas ?

3. Question based on Mass per cent, Molarity, Mole fraction, Molality

3.1(i) Define the following terms. (Write the mathematical formulas related to terms)(a) Mass percent

(b) Molarity (c) Molality (d) Mole-fraction (e) Mass percent

(ii)Calculate the mass of sodium acetate (CH_3COONa) required to make 500 mL of 0.375 molar aqueous solution. (Molar mass of sodium acetate is 82.0245 g mol^{-1}).

3.2 Calculate the concentration of nitric acid in moles per litre in a sample which has a density, 1.41 g mL^{-1} and the mass per cent of nitric acid in it being 69%.

3.3 What is the concentration of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) in mol L^{-1} if its 20 g are dissolved in enough water to make a final volume up to 2L?

3.4 If the density of methanol is 0.793 kg L^{-1} , what is its volume needed for making 2.5 L of its 0.25 M solution?

3.5 A sample of drinking water was found to be severely contaminated with chloroform, CHCl_3 , supposed to be carcinogenic in nature. The level of contamination was 15 ppm (by mass).

(i) Express this in percent by mass. (ii) Determine the molality of chloroform in the water sample.

3.6 The density of 3 M solution of NaCl is 1.25 g mL^{-1} . Calculate molality of the solution.

3.7 How are 0.50 mol Na_2CO_3 and 0.50 M Na_2CO_3 different?

3.8 Which one of the following will have largest number of atoms?

(i) 1 g Au (s) (ii) 1 g Na (s) (iii) 1 g Li (s)(iv) 1 g of Cl_2 (g)

3.9 Calculate the molarity of a solution of ethanol in water in which the mole fraction of ethanol is 0.040 (assume the density of water to be one).

3.10 Calculate the number of atoms in each of the following (i) 52 moles of Ar (ii) 52 u of He (iii) 52 g of He.

3.11 Calculate the molarity of NaOH in the solution prepared by dissolving its 4 g in enough water to form 250 mL of the solution.

3.12 A solution is prepared by adding 2 g of a substance A to 18 g of water. Calculate the mass per cent of the solute.

3.13 How does molality & Molarity depend on temperature? Out of molality & Molarity which one is better way to express concentration?

ANSWERS

2.1 Calculate the molecular mass of the following:

Ans: (i) $\text{H}_2\text{O} = 18$ (ii) $\text{CO}_2 = 44$ (iii) $\text{CH}_4 = 16$ (iv) $\text{C}_6\text{H}_{12}\text{O}_6 = 180$

2.2 Calculate the mass per cent of different elements present in sodium sulphate (Na_2SO_4).

Ans % Na = $46 \times 100/142 = 32.4$, % S = $32 \times 100/142 = 22.53$, % O = $64 \times 100/142 = 45.1$

2.3 Determine the empirical formula of an oxide of iron which has 69.9% iron and 30.1% Dioxygen by mass.

Ans: no of moles of Fe: $69.9/56 = 1.248$

no of moles of O = $30.1/16 = 1.881$

whole number ratio between the number of moles = 1: 1.5 = 2: 3.

Hence empirical formula is Fe_2O_3

2.4 How much copper can be obtained from 100 g of copper sulphate (CuSO_4)?

Ans: 63.5g of Cu in 159.5g of CuSO_4 .

$63.5 \times 100 / 159.5 = 39.81$ g of Cu in 100g of CuSO_4

2.5 In a reaction $\text{A} + \text{B}_2 \rightarrow \text{AB}_2$ Identify the limiting reagent, if any, in the following reaction mixtures.

(i) 300 atoms of A + 200 molecules of B Ans: B is limiting

(ii) 2 mol A + 3 mol B Ans: A is limiting

(iii) 100 atoms of A + 100 molecules of B Ans: reactants totally consumed

(iv) 5 mol A + 2.5 mol B Ans: B is limiting

(v) 2.5 mol A + 5 mol B Ans: A is limiting

2.6 Calculate the atomic mass (average) of chlorine using the following data:

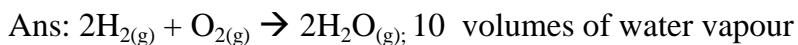
| Isotope | % Natural Abundance | Molar Mass |
|------------------|---------------------|------------|
| ^{35}Cl | 75.77 | 34.9689 |
| ^{37}Cl | 24.23 | 36.9659 |

$$\text{Ans: } (34.9689 \times 75.77) + (36.9659 \times 24.23) / 100 = 35.48$$

2.7 In three moles of ethane (C_2H_6), calculate the following:

- Number of moles of carbon atoms. Ans: $3 \times 2 = 6$
- Number of moles of hydrogen atoms. Ans: $3 \times 6 = 18$
- Number of molecules of ethane. Ans: $3 \times 6.023 \times 10^{23} = 18.069 \times 10^{23}$

2.8 If ten volumes of dihydrogen gas reacts with five volumes of dioxygen gas, how many volumes of water vapour would be produced?



2.9 A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide, 0.690 g of water and no other products. A volume of 10.0 L (measured at STP) of this welding gas is found to weigh 11.6 g. Calculate (i) empirical formula, (ii) molar mass of the gas, and (iii) molecular formula.

Ans:

- 12g of C in 44g of $\text{CO}_2 \Rightarrow (12/44) \times 3.38\text{g of C in } 3.38\text{g of CO}_2 = 0.922$
2g of H in 18g of $\text{H}_2\text{O} \Rightarrow (2/18) \times 0.690 \text{ of H in } 0.690\text{g of H}_2\text{O} = 0.077$
No of Moles of C = $0.922/12 = 0.077$
No of moles of H = 0.077
The empirical formula = CH
- 22.4L at STP = 1 molar mass
10L at STP weighs 11.6g;
 $22.4\text{L will weigh } (11.6/10) \times 22.4 = 26$
- Empirical formula mass = 13
Molecular mass = 26
The ratio of molecular mass: empirical formula mass = 2
Hence molecular formula is C_2H_2

2.10 Calculate the amount of water (g) produced by the combustion of 16 g of methane.

Ans: $\text{CH}_4 + 2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2$; 16g CH₄ is 1mole. From the stoichiometric equation we get 1mole of methane gives 2moles of H₂O. ie is $18 \times 2 = 36$ g of water.

2.11 How many moles of methane are required to produce 22 g CO₂ (g) after combustion?

Ans: 22g of CO₂ is $22/44$ moles ie 0.5 moles; 1mole of CH₄ produces 1mole of CO₂. Hence 0.5 moles of methane is required.

2.12 A compound contains 4.07 % hydrogen, 24.27 % carbon and 71.65 % chlorine.

Its molar mass is 98.96 g. What are its empirical and molecular formulas ?

Ans: no of moles of H = $4.07/1 = 4.07$; C = $24.27/12 = 2.02$; Cl = $71.65/35.5 = 2.02$

Simplest whole number ratio H: C:Cl = 2:1:1

Hence empirical formula is CH₂Cl

3. Question based on Mass per cent, Molarity, Mole fraction, Molality

3.1

(ii) Calculate the mass of sodium acetate (CH₃COONa) required to make 500 mL of 0.375 molar aqueous solution. (Molar mass of sodium acetate is 82.0245 g mol⁻¹).

Ans: no of moles of sodium acetate (CH₃COONa) required = $(0.375/1000) \times 500 = 0.1875$, ie $0.1875 \times 82.0245 \text{ g} = 15.38\text{g}$

3.2 Calculate the concentration of nitric acid in moles per litre in a sample which has a density, 1.41 g mL⁻¹ and the mass per cent of nitric acid in it being 69%.

Ans: 69g of HNO₃ in 100g of sample. $\Rightarrow 69/63 = 1.095$ moles in 100g of sample. $\Rightarrow 1.095$ moles in $100/1.41\text{ml}$ of acid i.e 70.92ml.

No of moles of HNO₃ in 1000ml = $(1.095/70.92) \times 1000 = 15.44\text{M}$

3.3 What is the concentration of sugar (C₁₂H₂₂O₁₁) in mol L⁻¹ if its 20 g are dissolved in enough water to make a final volume up to 2L?

Ans: 20g in 2lit \rightarrow 10g in 1 lit; $10/342 = 0.02924$ moles /lit

3.4 If the density of methanol is 0.793 kg L⁻¹, what is its volume needed for making 2.5 L of its 0.25 M solution?

Ans: moles of methanol required to prepare 2.5L of 0.25M methanol solution = $2.5 \times 0.25 = 0.625$ →
0.625 × 32g = 20g of methanol.

793g of methanol is present in 1000ml. => 20g is present in $(1000/793) \times 20$ ml of methanol sample.
25.22ml of methanol is used to prepare 2.5lit of 0.25M methanol.

3.5 A sample of drinking water was found to be severely contaminated with chloroform, CHCl_3 , supposed to be carcinogenic in nature. The level of contamination was 15 ppm (by mass).

(i) Express this in percent by mass. Ans: $(15/10^6) \times 100 = 15 \times 10^{-4}\%$ by mass

(ii) Determine the molality of chloroform in the water sample. Ans: Mass of solute in 1kg of solvent is 15×10^{-3} g. => $15 \times 10^{-3} / 119.5 = 1.26 \times 10^{-4}$ molal.

3.6 The density of 3 M solution of NaCl is 1.25 g mL^{-1} . Calculate molality of the solution.

Ans: $1.25 \text{ g/ml} \rightarrow 1250 \text{ g/lit}$. Mass of 1 litre solution is 1250g of which $3 \times 58.5 \text{ g} = 175.5 \text{ g}$ is solute. Mass of solvent = $1250 - 175.5 = 1074.5 \text{ g}$.

3moles of solute in 1.074kg of solvent → $3/1.074$ moles in 1kg of solvent. Hence
molality = 2.79moles/kg

3.8 Which one of the following will have largest number of atoms?

(i) 1 g Au (s) (ii) 1 g Na (s) (iii) 1 g Li (s) (iv) 1 g of $\text{Cl}_2(\text{g})$

Ans: iii) 1 g Li, because it has the least atomic mass among the given ones.

3.9 Calculate the molarity of a solution of ethanol in water in which the mole fraction of ethanol is 0.040 (assume the density of water to be one).

Ans: we have to calculate no of moles per litre. Let no of moles of ethanol be X. let 1 litre of water = 1kg of water. Then:

$$X/(X + 55.56) = 0.04 ; \text{let } X \ll 55.56 \text{ then } X/55.56 = 0.04 ; X = 2.22,$$

Hence molarity is 2.22moles /lit

3.10 Calculate the number of atoms in each of the following

(i) 52 moles of Ar; Ans: $52 \times 6.022 \times 10^{23} = 313.144 \times 10^{23} = 3.13 \times 10^{25}$ atoms

(ii) 52 u of He; Ans: $52/4 = 13$ atoms

(iii) 52 g of He; Ans: $(52/4) \times 6.022 \times 10^{23} = 78.286 \times 10^{23}$ atoms of He.

3.11 Calculate the molarity of NaOH in the solution prepared by dissolving its 4 g in enough water to form 250 mL of the solution.

Ans: 4g in 250ml \rightarrow 16g in 1 lit. \rightarrow $16/40 \text{ moles/lit} = 0.4 \text{ moles/lit} = 0.4M$

3.12 A solution is prepared by adding 2 g of a substance A to 18 g of water. Calculate the mass per cent of the solute.

Ans: $(2/18) \times 100$ is the mass percent.

2. Structure of Atom

Some Important Points and Terms of the Chapter

1. The word ‘atom’ has been derived from the Greek word ‘**a-tomio**’ which means ‘uncuttable’ or ‘non-divisible’.
2. J. J. Thomson, in 1898, proposed that an atom possesses a spherical shape (radius approximately 10–10 m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement (Fig. 2.4, NCERT Page 5). Many different names are given to this model, for example, **plum pudding, raisin pudding or watermelon.**
3. **Rutherford’s Nuclear Model of Atom:**
 - a) Most of the space in the atom is empty as most of the a-particles passed through the foil undeflected.
 - b) A few positively charged a-particles were deflected. The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had presumed. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged a-particles.
 - c) Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The radius of the atom is about 10^{-10} m, while that of nucleus is 10^{-15} m.
 - d) On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom (after the discovery of protons). According to this model : (i) The positive charge and most of the mass of the atom was densely concentrated in extremely small region. This very small portion of the atom was called nucleus by Rutherford. (ii) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits. Thus, Rutherford’s model of atom resembles the solar system in which the nucleus plays the role of sun and the electrons that of revolving planets. (iii) Electrons and the nucleus are held together by electrostatic forces of attraction.

4. The number of protons present in the nucleus is equal to atomic number (Z). the nucleus is equal to atomic number (Z) .i.e. **Atomic number (Z)** = number of protons in the nucleus of an atom = number of electrons in a neutral atom
5. Protons and neutrons present in the nucleus are collectively known as nucleons. The total number of nucleons is termed as **mass number (A)** of the atom. mass number (A) = number of protons (Z) + number of neutrons (n)
6. **Isobars** are the atoms with same mass number but different atomic number for example, ${}^6\text{C}^{14}$ and ${}^7\text{N}^{14}$. On the other hand, atoms with identical atomic number but different atomic mass number are known as **Isotopes**. e.g. ${}^6\text{C}^{14}$ ${}^6\text{C}^{13}$ ${}^6\text{C}^{12}$ & ${}^{17}\text{Cl}^{35}$, ${}^{17}\text{Cl}^{37}$
7. **Drawbacks of Rutherford Model** According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation (This feature does not exist for planets since they are uncharged). Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink. Calculations show that it should take an electron only 10^{-8} s to spiral into the nucleus. But this does not happen. Thus, the Rutherford model cannot explain the stability of an atom.
8. The frequency (ν), wavelength (λ) and velocity of light (c) are related by the equation (2.5). $c = \nu \lambda$ The other commonly used quantity specially in spectroscopy, is the wavenumber (v^-). It is defined as the number of wavelengths per unit length. Its units are reciprocal of wavelength unit, i.e., m^{-1} .
9. H. Hertz performed a very interesting experiment in which electrons (or electric current) were ejected when certain metals (for example potassium, rubidium, caesium etc.) were exposed to a beam of light . The phenomenon is called Photoelectric effect. **For photoelectric effect :** $h\nu = h\nu^0 + 1/2 m\nu^2$
10. **Planck's quantum theory.** (i) The energy is radiated or absorbed by a body not continuously but discontinuously in form of small packets. (ii) Each packet is called quantum. In case of light, the quantum is called ‘photon’. The energy of quantum is directly proportional to the frequency (ν) of the radiation. $E \propto \nu E = h\nu$, Where ‘ h ’ is Planck’s constant. Its value is 6.625×10^{-34} Joule second.
11. The spectrum of radiation emitted by a substance that has absorbed energy is called an **emission spectrum**. Atoms, molecules or ions that have absorbed radiation are said to be “excited”. To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted, as the sample gives up the absorbed energy, is recorded.

12. An **absorption spectrum** is like the photographic negative of an emission spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths.
13. **Line Spectrum of Hydrogen:** When an electric discharge is passed through gaseous hydrogen, the H₂ molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of discrete frequencies. The hydrogen spectrum consists of several series of lines named after their discoverers.

| Series | n ₁ | n ₂ | Spectral region |
|-----------------|----------------|----------------|-----------------|
| Lyman | 1 | 2,3..... | Ultraviolet |
| Balmer | 2 | 3,4..... | Visible |
| Paschen | 3 | 4,5..... | Infrared |
| Brackett | 4 | 5,6..... | Infrared |
| Pfund | 5 | 6,7..... | Infrared |

The Swedish spectroscopist, Johannes Rydberg, noted that all series of lines in the hydrogen spectrum

$$\bar{v} = 109,677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1}$$

could be described by the following expression :

14. Bohr's Model For Hydrogen Atom

- a) The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called orbits, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.
- b) An electron can move only in those orbits for which its angular momentum is integral multiple of $h/2\pi$ that is why only certain fixed orbits are allowed. The angular momentum of an electron in a given stationary state can be expressed as in equation

$$m_e v r = n \cdot \frac{h}{2\pi} \quad n = 1, 2, 3, \dots$$

- c) The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state. The energy change does not take place in a continuous manner.
- d) The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE , is given by :

$$v = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

15. Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom. For example, He^+ , Li^{2+} , Be^{3+} and so on. The energies of the stationary states associated with these kinds of ions (also known as hydrogen like species) are given by the

$$E_n = -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2} \right) \text{J}$$

and radii by the expression

$$r_n = \frac{52.9(n^2)}{Z} \text{ pm}$$

expression

16. **Limitations of Bohr's Model:** It fails to account for the finer details (doublet, that is two closely spaced lines) of the hydrogen atom spectrum observed by using sophisticated spectroscopic techniques. This model is also unable to explain the spectrum of atoms other than hydrogen, for example, helium atom which possesses only two electrons. Further, Bohr's theory was also unable to explain the splitting of spectral lines in the presence of magnetic field (**Zeeman effect**) or an electric field (**Stark effect**).

17. **Dual Behaviour of Matter:** The French physicist, de Broglie in 1924 proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle and wavelike properties.

18. The **de Broglie relation.** :de Broglie relation state that the wavelength associated with a moving object or an electron is inversely proportional to the momentum of the particle.

$$\lambda = \frac{h}{mv} = \frac{h}{p} \text{ where } p \text{ is the momentum of particle} = mv.$$

19. **Heisenberg's Uncertainty Principle.** It is not possible to determine the position and velocity simultaneously for a sub-atomic particle like electron at any given instant to an arbitrary degree of precision. Consequently, it is not possible to talk of path of the electron in which it moves. If ' Δx ' is uncertainty in position and ' ΔP ' is uncertainty in momentum then

$$\Delta x \cdot \Delta P \geq \frac{h}{4\pi}$$

20. **Orbital.** It is a region or space where there is maximum probability of getting electron.

21. **Quantum numbers.** They are used to get complete information about electron, i.e., location, energy, spin, etc. These quantum numbers also help to designate the electron present in an orbital.

22. **Principal quantum number.** It specifies the location and energy of an electron. It is measure of the effective volume of the electron cloud. It is denoted by ' n '. Its possible values are 1, 2, 3, 4

23. Angular momentum quantum number. It is also called ‘azimuthal quantum number’. It determines the shape of the orbital. It is denoted by ‘ l ’. The permitted values of ‘ l ’ are 0, 1, 2, etc., upto $n-1$. For a given value of n , $l = 0$ to $n-1$. e.g., if value of n is 4, l can have values 0, 1, 2, 3. It determines angular momentum. $mvr = \sqrt{l(l+1)} \frac{h}{2\pi}$

24. Magnetic quantum number. It is denoted by ‘ m ’ and its value depends on value of ‘ l ’ since magnetism is due to angular momentum. It determines the magnetic orientation of an orbital, i.e., the direction of orbital relative to magnetic field in which it is placed. Its permitted values are $-l$ to $+l$ including zero, e.g., when $l = 1$, then $m = -1, 0, +1$. It has total number of values equal to $2l + 1$.

25. Spin quantum number. It indicates, the direction in which electron revolves. Spin is magnetic property and is also quantized. It has two permitted values $+\frac{1}{2}$ or $-\frac{1}{2}$. The spin angular momentum of an electron is constant and cannot be changed.

26. (n+l) rule: The relative order of energies of various sub-shells in a multi-electron atom can be predicted with the help of (n+l) rule (also called Bohr-Bury rule) According to this rule a sub-shell with lower values of (n+l) has lower energy. In case two sub-shell has equal value of (n+l), the sub-shell with lower value of n has lower energy

27. Pauli’s Exclusion Principle. No two electrons in an atom can have all the four quantum numbers same. It can also be stated as – An orbital can have maximum two electrons and they must be of opposite spin quantum numbers.

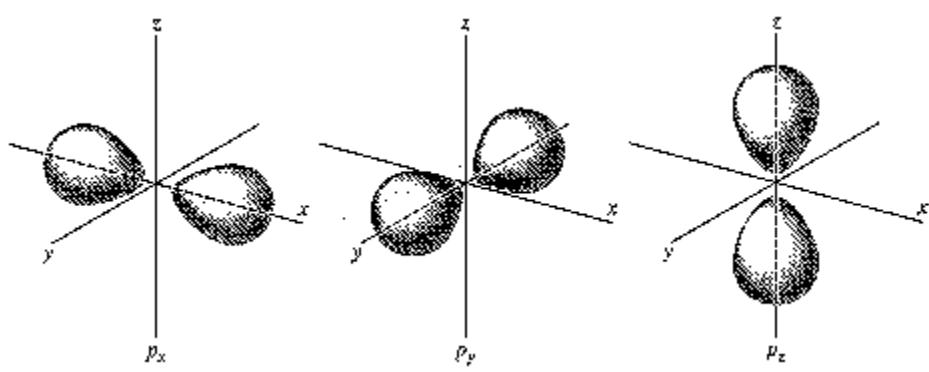
28. Aufbau principle. Electrons are filled in the various orbitals in the increasing order of their energies, i.e., orbital having lowest energy will be filled first and the orbital having highest energy will be filled last. **Increasing energy of atomic orbitals for multi-electron atoms**

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s$$

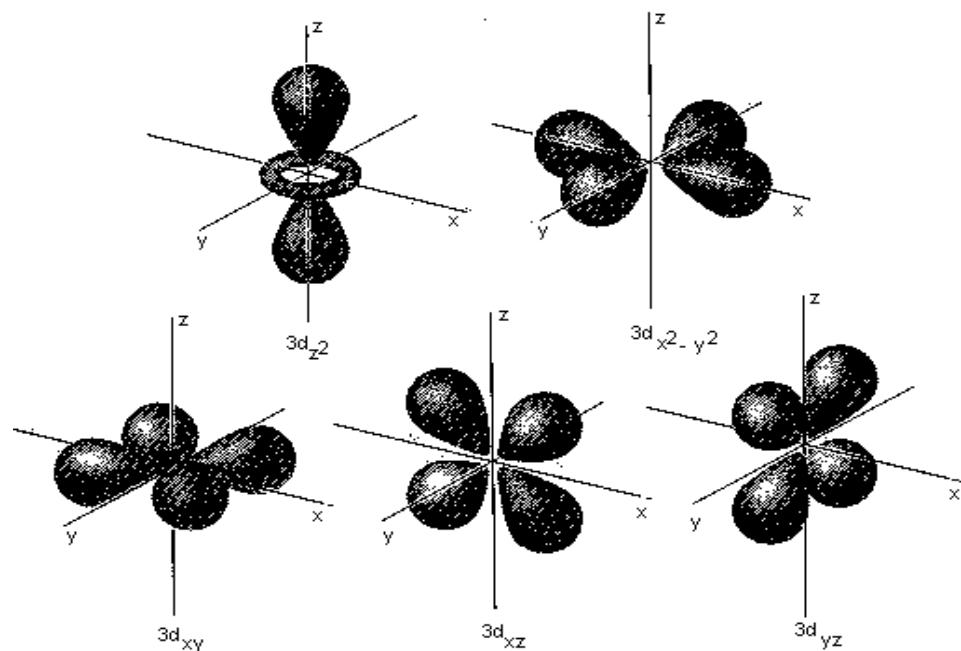
29. Hund’s rule of maximum multiplicity. No electron pairing takes place in p , d and f orbitals until each orbital in the given sub-shell contains one electron, e.g., N (7) has electronic configuration $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ according to Hund’s rule and not $1s^2 2s^2 2p_x^2 2p_y^1$.

30. The valence electronic configurations of Cr and Cu, therefore, are $3d^5 4s^1$ and $3d^{10} 4s^1$ respectively and not $3d^4 4s^2$ and $3d^9 4s^2$. It has been found that there is extra stability(Stability of Completely Filled and Half Filled Subshells) associated with these electronic configurations.

31. **Three orbitals of 2p subshell** ($2p_x$, $2p_y$, and $2p_z$ orbitals).



32. Five orbitals of 3d subshell ($3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals).



Unit-2

STRUCTURE OF ATOM

1. Questions based on sub-atomic particles (Electron, Protons and Neutrons) atomic models, Thomson Model Of Atom, Rutherford's Nuclear Model Of Atom. Atomic Number, Mass Number, Isobars, Isotopes, Drawbacks Of Rutherford Model.

1. Calculate the number of protons, neutrons and electrons in $^{35}\text{Br}^{80}$.
2. The number of electrons, protons and neutrons in a species are equal to 18,16 and 16 respectively. Assign the proper symbol to the species.
3. How many neutrons and protons are there in the following nuclei? $^6\text{C}^{13}$, $^8\text{O}^{16}$, $^{12}\text{Mg}^{24}$, $^{26}\text{Fe}^{56}$, $^{38}\text{Sr}^{88}$
4. Write the complete symbol for the atom with the given atomic number (Z) and atomic mass (A)
(i) Z = 17 , A = 35. (ii) Z = 92 , A = 233. (iii) Z = 4 , A = 9.
5. Which of the following are isoelectronic species i.e., those having the same number of electrons?
 Na^+ , K^+ , Mg^{2+} , Ca^{2+} , S^{2-} , Ar .
6. Give the number of electrons in the species H_2^+ , H_2 and O_2^+ .
7. Calculate the number of electrons which will together weigh one gram.
8. Calculate the mass and charge of one mole of electrons.
9. Compare Electron, Protons and Neutrons.
10. Describe Thomson Model Of Atom.
11. Explain Rutherford's scattering experiment.. What conclusions regarding the structure of atom were drawn by Rutherford on the basis of the observations of experiment? Give the major drawbacks of Rutherford Model.
12. In Rutherford's experiment, generally the thin foil of heavy atoms, like gold, platinum etc. have been used to be bombarded by the a-particles. If the thin foil of light atoms like aluminium etc. is used, what difference would be observed from the above results?
13. Define the terms Atomic Number, Mass Number, Isobars, Isotopes,

ANSWER

1. Calculate the number of protons, neutrons and electrons in ${}_{35}^{\text{Br}}{}^{80}$.

Ans: no of protons =no of electrons =35; no of neutrons= $80-35=45$

2. The number of electrons, protons and neutrons in a species are equal to 18,16 and 16 respectively. Assign the proper symbol to the species.

Ans: $[{}_{16}^{\text{S}}{}^{32}]^{2-}$

3. How many neutrons and protons are there in the following nuclei?

- ${}_{6}^{\text{C}}{}^{13}$, ans P=6, n=7
- ${}_{8}^{\text{O}}{}^{16}$,ans: P=8, n=8
- ${}_{12}^{\text{Mg}}{}^{24}$, Ans: P=12, n=12
- ${}_{26}^{\text{Fe}}{}^{56}$, Ans: P=26, n=30
- ${}_{38}^{\text{Sr}}{}^{88}$, Ans: P=38, n=50

4. Write the complete symbol for the atom with the given atomic number (Z) and atomic mass (A)

- Z = 17 , A = 35.Ans: ${}_{17}^{\text{Cl}}{}^{35}$
- Z = 92 , A = 233.Ans: ${}_{92}^{\text{U}}{}^{233}$
- Z = 4 , A = 9. Ans: ${}_{4}^{\text{Be}}{}^9$

5. Which of the following are isoelectronic species i.e., those having the same number of electrons? Na^+ , K^+ , Mg^{2+} , Ca^{2+} , S^{2-} , Ar.

Ans: i) Na^+ , Mg^{2+} ,
ii) K^+ , Ca^{2+} , S^{2-} , Ar are isoelectronic.

6. Give the number of electrons in the species H_2^+ , H_2 and O_2^+ .

Ans: 1,2,15

7. Calculate the number of electrons which will together weigh one gram.

Ans: mass of an electron: 9.1×10^{-28} g;

No of electrons weighing 1 g= $1 / 9.1 \times 10^{-28} = 1.1 \times 10^{27}$

8. Calculate the mass and charge of one mole of electrons.

Ans: mass of 1 electron: 9.1×10^{-28} g; mass of 1 mole of electrons: 9.1×10^{-28} g $\times 6.022 \times 10^{23}$
 $= 54.8 \times 10^{-5}$ g

Charge on an electron = 1.6×10^{-19} C

Charge on one mole of electrons = $1.6 \times 10^{-19} \times 6.022 \times 10^{23} = 9.635 \times 10^4 = 96500$ coulombs = 1 faraday

2. Questions based on frequency wavelength wavenumber threshold frequency and work function (W_0), Photoelectric effect, Emission and Absorption Spectra, Line Spectrum of Hydrogen, Bohr's model for hydrogen atom, radii of the stationary states, energy of stationary state, Limitations of Bohr's Model

1. Define the terms frequency wavelength & wave number (Write mathematical forms also).
2. The Vividh Bharati station of All India Radio, Delhi, broadcasts on a frequency of 1,368 kHz (kilo hertz). Calculate the wavelength of the electromagnetic radiation emitted by transmitter. Which part of the electromagnetic spectrum does it belong to?
3. The wavelength range of the visible spectrum extends from violet (400 nm) to red (750 nm). Express these wavelengths in frequencies (Hz). ($1\text{nm} = 10^{-9}$ m)
4. Calculate (a) wavenumber and (b) frequency of yellow radiation having wavelength 5800\AA .
5. Yellow light emitted from a sodium lamp has a wavelength of 580 nm. Calculate the frequency and wavenumber of the yellow light.
6. Find energy of each of the photons which (i) correspond to light of frequency 3×10^{15} Hz. (ii) have wavelength of 0.50\AA .
7. Calculate the wavelength, frequency and wave number of a light wave whose period is 2.0×10^{-10} s.
8. Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800\AA . Calculate threshold frequency (v_0) and work function (W_0) of the metal.
9. Explain Photoelectric effect, Emission and Absorption Spectra
10. Give the postulates of Bohr's model. also write its Limitations.
11. Write a note on the Spectral Lines for Atomic Hydrogen.
12. What are the frequency and wavelength of a photon emitted during a transition from $n = 5$ state to the $n = 2$ state in the hydrogen atom?
13. Calculate the energy associated with the first orbit of He^+ . What is the radius of this orbit?

14. What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with $n = 4$ to an energy level with $n = 2$?

15 How much energy is required to ionise a H atom if the electron occupies $n = 5$ orbit? Compare your answer with the ionization enthalpy of H atom (energy required to remove the electron from $n = 1$ orbit).

16. What is the maximum number of emission lines when the excited electron of a H atom in $n = 6$ drops to the ground state?

17.(i) The energy associated with first orbit in the hydrogen atom is $-2.18 \times 10^{-18} \text{ J atom}^{-1}$. What is the energy associated with the fifth orbit?

(ii) Calculate the radius of Bohr's fifth orbit for hydrogen atom.

18. Calculate the wavenumber for the longest wavelength transition in the Balmer series of atomic hydrogen.

19. What is the energy in joules, required to shift the electron of the hydrogen atom from the first Bohr orbit to the fifth Bohr orbit and what is the wavelength of the light emitted when the electron returns to the ground state? The ground state electron energy is $-2.18 \times 10^{-11} \text{ ergs}$.

20. The electron energy in hydrogen atom is given by $E_n = (-2.18 \times 10^{-18})/n^2 \text{ J}$. Calculate the energy required to remove an electron completely from the $n = 2$ orbit. What is the longest wavelength of light in cm that can be used to cause this transition?

21. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum?

ANSWER

2.The Vividh Bharati station of All India Radio, Delhi, broadcasts on a frequency of 1,368 kHz (kilo hertz). Calculate the wavelength of the electromagnetic radiation emitted by transmitter. Which part of the electromagnetic spectrum does it belong to?

$$\text{Ans: } v = 1.368 \times 10^6 = c/\lambda \Rightarrow \lambda = 3 \times 10^8 / 1.368 \times 10^6 = 219 \text{ m.}$$

3. The wavelength range of the visible spectrum extends from violet (400 nm) to red (750 nm). Express these wavelengths in frequencies (Hz). ($1 \text{ nm} = 10^{-9} \text{ m}$)

$$\text{Ans: } v = c/\lambda = 3 \times 10^8 / 400 \times 10^{-9} = 7.5 \times 10^{14} \text{ hertz}$$

$$v = c/\lambda = 3 \times 10^8 / 750 \times 10^{-9} = 4 \times 10^{14} \text{ hertz}$$

4. Calculate(a) wavenumber and (b) frequency of yellow radiation having wavelength 5800 \AA .

$$\text{Ans: } v = c/\lambda = 3 \times 10^8 / 5800 \times 10^{-10} = 5.17 \times 10^{14} \text{ hertz}$$

$$\text{Wave number (v)} = 1/\lambda = 1/5.8 \times 10^{-7} = 1.72 \times 10^6$$

5. Yellow light emitted from a sodium lamp has a wavelength of 580 nm. Calculate the frequency and wavenumber of the yellow light.

$$\text{Ans: } v = c/\lambda = 3 \times 10^8 / 5800 \times 10^{-10} = 5.17 \times 10^{14} \text{ hertz}$$

$$\text{Wave number (v)} = 1/\lambda = 1/5.8 \times 10^{-7} = 1.72 \times 10^6$$

6. Find energy of each of the photons which

(i) correspond to light of frequency $3 \times 10^{15} \text{ Hz}$.

$$\text{Ans: } E = h v = 6.6 \times 10^{-34} \times 3 \times 10^{15} = 1.98 \times 10^{-18} \text{ Joules}$$

(ii) have wavelength of 0.50 Å.

$$\text{Ans: } E = hc/\lambda = 6.6 \times 10^{-34} \times 3 \times 10^8 / 0.5 \times 10^{-10} = 19.8 / 5 \times 10^{-15} \text{ Joules} = 3.96 \times 10^{-15} \text{ Joules}$$

7. Calculate the wavelength, frequency and wave number of a light wave whose period is $2.0 \times 10^{-10} \text{ s}$.

$$\text{Ans: } 1/T = 1/2 \times 10^{-10} = v;$$

$$v = c/\lambda;$$

$$\lambda = c/v = 3 \times 10^8 / 5 \times 10^{-10} = 6 \times 10^{-2} \text{ m}$$

$$\text{Wave number (v)} = 1/\lambda = 1/6 \times 10^{-2} = 167 \text{ m}^{-1}$$

8. Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800 Å. Calculate threshold frequency (v_0) and work function (W_0) of the metal.

$$\text{Ans: : work function} = hc/\lambda = 6.6 \times 10^{-34} \times 3 \times 10^8 / 6.8 \times 10^{-7} = 2.912 \times 10^{-19} \text{ Joules}$$

$$\text{Threshold frequency} = c/\lambda = 3 \times 10^8 / 6.8 \times 10^{-7} = 4.4 \times 10^{14}$$

12. What are the frequency and wavelength of a photon emitted during a transition from $n = 5$ state to the $n = 2$ state in the hydrogen atom?

$$\text{Ans: } E = -1312(1/5^2 - 1/2^2) = hc/\lambda \text{ in kJoules/mole} = 1312 \times 21 \times 10^3 / 100 \times 6.022 \times 10^{23}$$

$$\begin{aligned} \lambda &= hc/E = 6.6 \times 10^{-34} \times 3 \times 10^8 \times 100 \times 6.022 \times 10^{23} / 1312 \times 21 \times 10^3 = 19.8 \times 6.6 \times 10^{-1} / 27552 \\ &= 4.743 \times 10^{-7} \text{ m} = 4743 \times 10^{-10} \end{aligned}$$

Wavelength of the emitted photon is 4743 Å

$$v = c/\lambda$$

$$v = 3 \times 10^8 / 4.743 \times 10^{-7} = 6.325 \times 10^{14}$$

13. Calculate the energy associated with the first orbit of He^+ . What is the radius of this orbit?

$$E = -2.18 \times 10^{-18} Z^2 / n^2 \text{ J} = -2.18 \times 10^{-18} \times 2^2 / 1^2 = -8.72 \times 10^{-18} \text{ J}$$

14. What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with $n = 4$ to an energy level with $n = 2$?

$$E = -2.18 \times 10^{-18} (1/2^2 - 1/4^2)$$

$$= -2.18 \times 10^{-18} \times 3/16 = -0.40875 \times 10^{-18}$$

$E = -0.40875 \times 10^{-18}$ → energy is released.

$$E = hc/\lambda = 6.6 \times 10^{-34} \times 3 \times 10^8 / \lambda$$

$$\lambda = 6.6 \times 10^{-34} \times 3 \times 10^8 / 0.40875 \times 10^{-18} = 48.44 \times 10^{-8} \text{ m} = 4844 \text{ Å}$$

15 How much energy is required to ionize a H atom if the electron occupies $n = 5$ orbit? Compare your answer with the ionization enthalpy of H atom (energy required to remove the electron from $n = 1$ orbit).

$$E_5 = -2.18 \times 10^{-18} / 5^2 = -8.72 \times 10^{-20} \text{ J}$$

$E_1 = -2.18 \times 10^{-18}$. Ionization energy of 1 H atom is 25 times the energy required to remove an electron from $n=5$.

16. What is the maximum number of emission lines when the excited electron of a H atom in $n = 6$ drops to the ground state?

Ans: $5+4+3+2+1=15$ lines

17.(i) The energy associated with first orbit in the hydrogen atom is $-2.18 \times 10^{-18} \text{ J atom}^{-1}$. What is the energy associated with the fifth orbit?

(ii) Calculate the radius of Bohr's fifth orbit for hydrogen atom.

$$R = 52.9(n^2)/z = 52.9 \times 25/1 = 1322.5 \text{ pm}$$

18. Calculate the wave number for the longest wavelength transition in the Balmer series of atomic hydrogen.

$$\bar{v} = 109,677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1}$$

longest wavelength is minimum energy ie $3 \rightarrow 4$ transition

$$= 109677(1/3^2 - 1/4^2)$$
$$= 109677 \times 5/36 = 15233 \text{ cm}^{-1}$$

$$\Lambda = 6.565 \times 10^{-5} \text{ cm} = 6.565 \times 10^{-7} \text{ m} = 6565 \text{ Å}$$

19. What is the energy in joules, required to shift the electron of the hydrogen atom from the first Bohr orbit to the fifth Bohr orbit and what is the wavelength of the light emitted when the electron returns to the ground state? The ground state electron energy is -2.18×10^{-11} ergs.

$$\text{Ans: } E = 2.18 \times 10^{-11} (1/5^2 - 1/1^2)$$

$$E = 2.18 \times 10^{-11} (24/25) = 2.09 \times 10^{-11} \text{ ergs.} = 2.09 \times 10^{-18} \text{ J}$$

$$\Lambda = hc/E = 6.6 \times 10^{-34} \times 3 \times 10^8 / 2.09 \times 10^{-18} = 9.474 \times 10^{-8} \text{ m} = 947.4 \text{ Å. This falls in the uv range}$$

20. The electron energy in hydrogen atom is given by $E_n = (-2.18 \times 10^{-18})/n^2 \text{ J}$. Calculate the energy required to remove an electron completely from the $n = 2$ orbit. What is the longest wavelength of light in cm that can be used to cause this transition?

$$\text{Ans: } E_2 = 2.18 \times 10^{-18} / 4 = 5.36 \times 10^{-19} \text{ J}$$

$$\Lambda = hc/E = 6.6 \times 10^{-34} \times 3 \times 10^8 / 5.36 \times 10^{-19} = 3.694 \times 10^{-7} \text{ m} = 3.694 \times 10^{-5} \text{ cm}$$

Ie light of minimum wavelength $3.694 \times 10^{-5} \text{ cm}$ is required to remove the electron from $n=2$

21. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum?

$$E = -2.18 \times 10^{-18} \times 2^2 \times (1/2^2 - 1/4^2) = 2.18 \times 10^{-18} \times 4 \times 3 / 16 = 1.635 \times 10^{-18} \text{ J}$$

$\Lambda = hc/E = 6.6 \times 10^{-34} \times 3 \times 10^8 / 1.635 \times 10^{-18} = 12.11 \times 10^{-8} \text{ m} = 1211 \text{ Å. This belongs to the uv range and hence the llyman series.}$

$$E = 2.18 \times 10^{-18} \times (1 - 1/n^2) = 2.18 \times 10^{-18} \times 12 / 16$$

$$1 - 1/n^2 = 12/16 = 3/4$$

$$1/n^2 = 1/4$$

Hence $n=2$. The transition $2 \rightarrow 1$ in the Hydrogen spectrum corresponds to the given energy transition.

3..Questions based on Dual behaviour of matter (de Broglie's relation), Heisenberg uncertainty principle.

1. Explain Dual behaviour of matter.
2. State de Broglie's relation. Give its mathematical expression.
3. What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 m s^{-1} ?
4. The mass of an electron is $9.1 \times 10^{-31} \text{ kg}$. If its K.E. is $3.0 \times 10^{-25} \text{ J}$, calculate its wavelength.
5. Calculate the mass of a photon with wavelength 3.6 Å .

6. The velocity associated with a proton moving in a potential difference of 1000 V is $4.37 \times 10^5 \text{ ms}^{-1}$. If the hockey ball of mass 0.1 kg is moving with this velocity, Calculate the wavelength associated with this velocity.
7. If the velocity of the electron in Bohr's first orbit is $2.19 \times 10^6 \text{ ms}^{-1}$, calculate the de Broglie wavelength associated with it.
8. Similar to electron diffraction, neutron diffraction microscope is also used for the determination of the structure of molecules. If the wavelength used here is 800 pm, calculate the characteristic velocity associated with the neutron.
9. Dual behaviour of matter proposed by de Broglie led to the discovery of electron microscope often used for the highly magnified images of biological molecules and other type of material. If the velocity of the electron in this microscope is $1.6 \times 10^6 \text{ ms}^{-1}$, calculate de Broglie wavelength associated with this electron.
10. Calculate the wavelength of an electron moving with a velocity of $2.05 \times 10^7 \text{ ms}^{-1}$
11. The mass of an electron is $9.1 \times 10^{-31} \text{ kg}$. If its K.E. is $3.0 \times 10^{-25} \text{ J}$, calculate its wavelength.
12. Why de Broglie's relation is not associated with ordinary objects.
13. State Heisenberg's Uncertainty Principle. Give its mathematical expression.
14. A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1 Å. What is the uncertainty involved in the measurement of its velocity?
15. If the position of the electron is measured within an accuracy of $\pm 0.002 \text{ nm}$, calculate the uncertainty in the momentum of the electron. Suppose the momentum of the electron is $h/4\pi \times 0.05 \text{ nm}$, is there any problem in defining this value.
16. Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the de Broglie wavelength associated with the electron revolving around the orbit.

ANSWER

3. What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 m s^{-1} ?

$$\text{Ans: } \lambda = h/mv = 6.6 \times 10^{-34} / 0.1 \times 10 = 6.6 \times 10^{-34} \text{ m}$$

4. The mass of an electron is $9.1 \times 10^{-31} \text{ kg}$. If its K.E. is $3.0 \times 10^{-25} \text{ J}$, calculate its wavelength.

$$\text{Ans: } KE = \frac{1}{2} mv^2 = 3 \times 10^{-25}; v^2 = 6 \times 10^{-25} = 60 \times 10^{-26} \Rightarrow v = 7.746 \times 10^{-13} \text{ m/s}$$

$$\lambda = h/mv = 6.6 \times 10^{-34} / 9.1 \times 10^{-31} \times 7.746 \times 10^{-13} = 9.363 \times 10^{-12} \text{ m}$$

5. Calculate the mass of a photon with wavelength 3.6 Å.

$$\text{Ans: } v = 3 \times 10^8 \text{ m/s}$$

$$\lambda = h/mv = 6.6 \times 10^{-34} / m \times 3 \times 10^8$$

$$m = h/v \lambda = 6.6 \times 10^{-34} / 3 \times 10^8 \times 3.6 \times 10^{-10} = 6.11 \times 10^{-33} \text{ kg}$$

6. The velocity associated with a proton moving in a potential difference of 1000 V is $4.37 \times 10^5 \text{ ms}^{-1}$. If the hockey ball of mass 0.1 kg is moving with this velocity, Calculate the wavelength associated with this velocity.

$$\lambda = h/mv = 6.6 \times 10^{-34} / 0.1 \times 4.37 \times 10^5 = 1.51 \times 10^{-38} \text{ m}$$

7. If the velocity of the electron in Bohr's first orbit is $2.19 \times 10^6 \text{ ms}^{-1}$, calculate the de Broglie wavelength associated with it.

$$\lambda = h/mv = 6.6 \times 10^{-34} / 9.1 \times 10^{-31} \times 2.19 \times 10^6 = 3.3 \times 10^{-10} \text{ m}$$

8. Similar to electron diffraction, neutron diffraction microscope is also used for the determination of the structure of molecules. If the wavelength used here is 800 pm, calculate the characteristic velocity associated with the neutron.

$$\lambda = h/mv = 6.6 \times 10^{-34} / 6.67 \times 10^{-27} \text{ kg} \times v = 8 \times 10^{-10}$$

$$v = 6.6 \times 10^{-34} / 6.67 \times 10^{-27} \text{ kg} \times 8 \times 10^{-10} = 125 \text{ m/s}$$

9. Dual behavior of matter proposed by de Broglie led to the discovery of electron microscope often used for the highly magnified images of biological molecules and other type of material. If the velocity of the electron in this microscope is $1.6 \times 10^6 \text{ ms}^{-1}$, calculate de Broglie wavelength associated with this electron.

$$\lambda = h/mv = 6.6 \times 10^{-34} / 9.1 \times 10^{-31} \times 1.6 \times 10^6 = 4.5 \times 10^{-10} \text{ m}$$

10. Calculate the wavelength of an electron moving with a velocity of $2.05 \times 10^7 \text{ ms}^{-1}$

$$\lambda = h/mv = 6.6 \times 10^{-34} / 9.1 \times 10^{-31} \times 2.05 \times 10^7 = 3.538 \times 10^{-10} \text{ m}$$

14. A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1 Å. What is the uncertainty involved in the measurement of its velocity?

$$\Delta x \cdot \Delta P \geq \frac{h}{4\pi}$$

$$\Delta x \cdot m \Delta v = h / 4\pi$$

$$\Delta v = h / 4\pi m \Delta x = 6.6 \times 10^{-34} / 4 \times 3.14 \times 9.1 \times 10^{-31} \times 10^{-11} = 5.77 \times 10^{-6} \text{ m/s}$$

15. If the position of the electron is measured within an accuracy of ± 0.002 nm, calculate the uncertainty in the momentum of the electron. Suppose the momentum of the electron is $h/4\pi \times 0.05$ nm, is there any problem in defining this value.

$$\Delta x \cdot \Delta P \geq \frac{h}{4\pi}$$

$$\Delta P = h / 4\pi X \Delta x$$

$$\Delta P = 6.6 \times 10^{-34} / 4 \times 3.14 \times 0.002 \times 10^{-9}$$

$$\Delta P = 2.69 \times 10^{-22} \text{ kg m/s}$$

4. QUESTIONS BASED ON QUANTUM NUMBERS, AUFBAU RULE, PAULI RULE, HUND'S RULE, ELECTRONIC CONFIGURATION OF ATOMS & IONS.

- What information is provided by the four quantum numbers?
 - Using s, p, d, f notations, describe the orbital with the following quantum numbers
(a) n = 2, l = 1, (b) n = 4, l = 0, (c) n = 5, l = 3, (d) n = 3, l = 2 (e) n=1, l=0 (f) n = 3 l=1 (g) n = 4; l=2 (h) n= 4; l=3.
 - What is the total number of orbitals associated with the principal quantum number n = 3?
 - What is the lowest value of n that allows g orbitals to exist?
 - An electron is in one of the 3d orbitals. Give the possible values of n, l and m_l for this electron.
 - (i) An atomic orbital has n = 3. What are the possible values of l and m_l?
(ii) List the quantum numbers (m_l and l) of electrons for 3d orbital.
(iii) Which of the following orbitals are possible? 1p, 2s, 2p, 2d, 4f ,6d and 3f.
 - Explain, giving reasons, which of the following sets of quantum numbers are not possible.
(a) n = 0, l = 0, m_l = 0, m_s = + ½ (b) n = 1, l = 0, m_l = 0, m_s = - ½ (c) n = 1, l = 1, m_l = 0, m_s = + ½ (d) n = 2, l = 1, m_l = 0, m_s = - ½ (e) n = 3, l = 3, m_l = -3, m_s = + ½ (f) n = 3, l = 1, m_l = 0, m_s = + ½
 - (i) How many electrons in an atom may have the following quantum numbers?
(a) n = 4, m_s = - ½ (b) n = 3, l = 0
(ii) How many sub-shells are associated with n = 4?
(iii) How many electrons will be present in the sub-shells having m_s value of -1/2 for n = 4?
 - State (n+l) rule Aufbau rule & Pauli rule.
 - Give the electronic configuration of first 30 elements.
 - Explain the exceptional configuration of copper and chromium.
 - Give the electronic configurations of the following ions: Cu²⁺ Cr³⁺ Fe²⁺ S²⁻ Fe²⁺ O²⁻ Na⁺

13. Explain Hunds rule of maximum multiplicity with an example.
14. Indicate the number of unpaired electrons in : (a) P, (b) Si, (c) Cr, (d) Fe and (e) Kr.
15. The quantum numbers of six electrons are given below. Arrange them in order of increasing energies. If any of these combination(s) has/have the same energy lists:
- (1). $n = 4, l = 2, m_l = -2, m_s = -1/2$ (2). $n = 3, l = 2, m_l = 1, m_s = +1/2$
- (3.) $n = 4, l = 1, m_l = 0, m_s = +1/2$ (4.) $n = 3, l = 2, m_l = -2, m_s = -1/2$
- (5). $n = 3, l = 1, m_l = -1, m_s = +1/2$ (6). $n = 4, l = 1, m_l = 0, m_s = +1/2$
16. (i) Write the electronic configurations of the following ions: (a) H^- (b) Na^+ (c) O^{2-} (d) F^-
- (ii) What are the atomic numbers of elements whose outermost electrons are represented by (a) $3s^1$ (b) $2p^3$ and (c) $3p^5$?
- (iii) Which atoms are indicated by the following configurations? (a) $[\text{He}] 2s^1$ (b) $[\text{Ne}] 3s^23p^3$ (c) $[\text{Ar}] 4s^23d^1$
17. An atom of an element contains 29 electrons and 35 neutrons. Deduce (i) the number of protons and (ii) the electronic configuration of the element.
18. Among the following pairs of orbitals which orbital will experience the larger effective nuclear charge? (i) 2s and 3s, (ii) 4d and 4f, (iii) 3d and 3p.
19. The unpaired electrons in Al and Si are present in 3p orbital. Which electrons will experience more effective nuclear charge from the nucleus?
- 20 The bromine atom possesses 35 electrons. It contains 6 electrons in 2p orbital, 6 electrons in 3p orbital and 5 electrons in 4p orbital. Which of these electron experiences the lowest effective nuclear charge?
21. Draw the shapes of s,p,d & f orbitals.

3. Classification of elements and periodicity in properties

Some Important Points and Terms of the Chapter

1. **Dobereiner's Triads:** In 1817 a German chemist Doberneiner identified certain groups of three elements. These groups of three elements having similar properties was called triads. When three elements were arranged in order of their increasing atomic masses, the atomic mass of the middle element was roughly the mean of the atomic masses of the other two elements.
2. **Newlands Law of octaves:** When elements were arranged in order of their increasing relative atomic masses. The properties of every eighth elements were similar to the first one, like the eighth note of a musical scale. This repetition in the properties of elements is just like the repetition of eighth node in an octave of music.
3. **Mendeleev's Periodic Law:** The physical and chemical properties of elements are the periodic function of their atomic masses.
4. **Mendeleev's Periodic Table:** When mendeleev started his work, 63 elements were known at that time. He selected hydrogen and oxygen as they are very reactive and formed compounds with most elements. Mendeleev's periodic table contains vertical columns called groups and horizontal rows called periods. There were 7 periods and 8 groups. Noble gases were not known at that time. So there was no group of noble gases. The elements in each group of the periodic tables are similar to one another in many properties. The similar properties of the elements are repeated periodically.

(a) Merits of mendeleev's classification

- Mendeleev's periodic law predicted the existence of some elements that had not been discovered at that time
- Could predict the properties of several elements on the basis of their position in the periodic table.
- Could accommodate noble gases when they were discovered.

(b) Limitations of mendeleev's classification :-

- The correct position could not be assigned to the hydrogen in the periodic table.
- Wrong order of the atomic masses of some elements could not be explained.

- The position of isotopes could not be explained.
- Uncertainty in prediction of new elements was there.

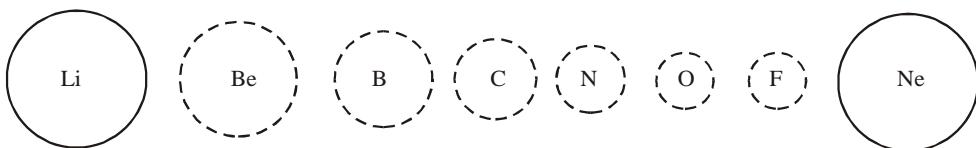
5. Modern periodic law: Properties of elements are the periodic function of their atomic number.

6. Modern Periodic Table: This table was prepared by Bohr and is based upon the electronic configuration of elements. The table consists of 18 vertical columns called groups. Elements having similar outer electronic configurations in their atoms are arranged in vertical columns, referred to as groups. According to the recommendation of International Union of Pure and Applied Chemistry (IUPAC), the groups are numbered from 1 to 18 and the table consists of 7 horizontal rows called periods. The first period contains 2 elements. The subsequent periods consist of 8, 8, 18, 18 and 32 elements, respectively. The seventh period is incomplete and like the sixth period would have a theoretical maximum (on the basis of quantum numbers) of 32 elements. In this form of the Periodic Table, 14 elements of both sixth and seventh periods (lanthanoids and actinoids, respectively) are placed in separate panels at the bottom

| group | period | | | | | | | | | | | | | | | | | | |
|-------|--------|----|--------|-------|-------|-------|-------|---------|-------|-------|-------|-------|------|-----|-----|-----|------|------------------|--|
| | | | | | | | | | | | | | | | | | 2 | 18 VIIIb 0 | |
| 1 | H | 2 | | | | | | | | | | | | | | | | | |
| 1 | Li | Be | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | He | |
| 2 | Na | Mg | IIIa** | IVa | Va | VIa | VIIa | IIIb*** | IVb | Vb | VIb | VIIb | IIIa | IVa | Va | Vb | VIIb | VIIa | |
| 3 | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | B | C | N | O | F | Ne | |
| 4 | Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | Al | Si | P | S | Cl | Ar | |
| 5 | Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Ga | Ge | As | Se | Br | Kr | |
| 6 | Fr | Ra | Ac | ***** | ***** | ***** | ***** | ***** | ***** | ***** | ***** | ***** | 58 | 59 | 60 | 61 | 62 | 63 | |
| 7 | | | | | | | | | | | | | Pr | Nd | Pm | Sm | Eu | Gd | |
| | | | | | | | | | | | | | Tb | Dy | Ho | Er | 67 | 68 | |
| | | | | | | | | | | | | | 65 | 66 | 69 | 70 | 71 | Lu | |
| | | | | | | | | | | | | | 90 | 91 | 92 | 93 | 94 | 95 | |
| | | | | | | | | | | | | | Am | Pu | Cm | Bk | Cf | 97 | |
| | | | | | | | | | | | | | Es | Fm | 100 | 101 | 102 | 103 | |
| | | | | | | | | | | | | | 101 | 102 | 103 | Yb | Lu | Lr | |

| Digit | Name | Abbreviation |
|-------|------|--------------|
| 0 | nill | n |
| 1 | un | u |
| 2 | bi | b |
| 3 | tri | t |
| 4 | quad | q |
| 5 | pent | p |
| 6 | hex | h |
| 7 | sept | s |
| 8 | oct | o |
| 9 | enn | e |

8. We can classify the elements into four blocks viz., s-block, p-block, d-block and f-block depending on the type of atomic orbital that are being filled with electrons.
9. **s-Block Elements** :The elements of Group 1 (alkali metals) and Group 2 (alkaline earth metals) which have ns^1 and ns^2 outermost electronic configuration belong to the s-Block Elements.
10. **p-Block Elements** The p-Block Elements comprise those belonging to Group 13 to 18 and these together with the s-Block Elements are called the Representative Elements or Main Group Elements. The outermost electronic configuration varies from ns^2np^1 to ns^2np^6 in each period.
11. **d-Block Elements** These are the elements of Group 3 to 12 in the centre of the Periodic Table. These are characterised by the filling of inner d orbitals by electrons and are therefore referred to as d-Block Elements. These elements have the general outer electronic configuration $(n-1)d^{1-10}ns^{0-2}$.
12. **f-Block Elements** The two rows of elements at the bottom of the Periodic Table, called the Lanthanoids, Ce($Z = 58$) – Lu($Z = 71$) and Actinoids, Th($Z = 90$) – Lr ($Z = 103$) are characterised by the outer electronic configuration $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$. The last electron added to each element is filled in f- orbital. These two series of elements are hence called the Inner-Transition Elements (f-Block Elements).
13. **Variation in Atomic Radius in Period:** The atomic size generally decreases across a period It is because within the period the outer electrons are in the same valence shell and the effective nuclear charge increases as the atomic number increases resulting in the increased attraction of electrons to the nucleus.



14. Variation in Atomic Radius in Group: Within a family or vertical column of the periodic table, the atomic radius increases regularly with atomic number as). as we descend the groups, the principal quantum number (n) increases and the valence electrons are farther from the nucleus. This happens because the inner energy levels are filled with electrons, which serve to shield the outer electrons from the pull of the nucleus. Consequently the size of the atom increases as reflected in the atomic radii.

15. The **atomic radii of noble gases** are not considered here. Being monatomic, their (non-bonded radii) values are very large. In fact radii of noble gases should be compared not with the covalent radii but with the van der Waals radii of other elements.

16. A **cation is smaller than its parent atom** because it has fewer electrons while its nuclear charge remains the same. **The size of an anion will be larger than that of the parent atom** because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge. For example, the ionic radius of fluoride ion (F^-) is 136 pm whereas the atomic radius of fluorine is only 64 pm. On the other hand, the atomic radius of sodium is 186 pm compared to the ionic radius of 95 pm for Na^+ .

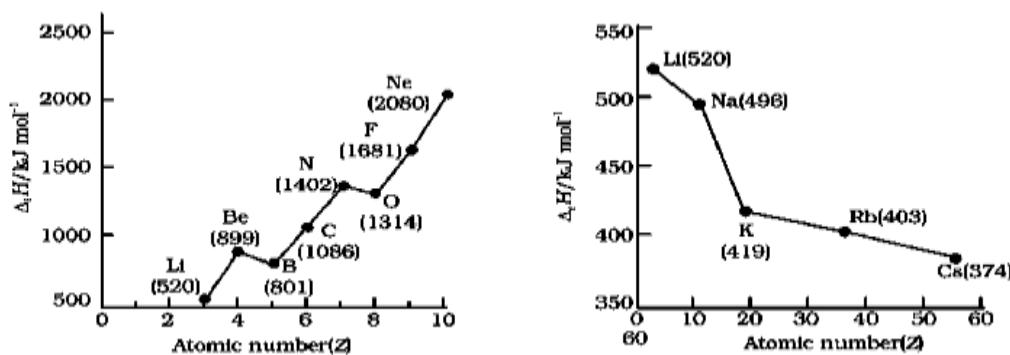
17. Isoelectronic species :Atoms and ions which contain the same number of electrons.. For example, O^{2-} , F^- , Na^+ and Mg^{2+} have the same number of electrons (10). Their radii would be different because of their different nuclear charges. The cation with the greater positive charge will have a smaller radius because of the greater attraction of the electrons to the nucleus. Anion with the greater negative charge will have the larger radius. In this case, the net repulsion of the electrons will outweigh the nuclear charge and the ion will expand in size.

18. Ionization Enthalpy: It represents the energy required to remove an electron from an isolated gaseous atom (X) in its ground state. In other words, the first ionization enthalpy for an element X is the enthalpy change (Δ_iH) for the reaction depicted in equation. $X(g) \rightarrow X^+(g) + e^-$. The ionization enthalpy is expressed in units of kJ mol^{-1} . We can define the second ionization enthalpy as the energy required to remove the second most loosely bound electron; it is the energy required to carry out the reaction shown in equation $X^+(g) \rightarrow X^{2+}(g) + e^-$. Energy is always required to remove electrons from an atom and hence ionization enthalpies are always positive. The second ionization enthalpy will be higher than the first ionization enthalpy because it is more difficult to remove an electron from a positively charged ion than from a neutral atom.

In the same way the third ionization enthalpy will be higher than the second and so on. The term “ionization enthalpy”, if not qualified, is taken as the first ionization enthalpy.

19. Variation in Ionization Enthalpy in Group: As we descend in a group the first ionization enthalpy generally decreases .Because as we go down a group, the outermost electron being increasingly farther from the nucleus, there is an increased shielding of the nuclear charge by the electrons in the inner levels. In this case, increase in shielding outweighs the increasing nuclear charge and the removal of the outermost electron requires less energy down a group.

20. Variation in Ionization Enthalpy in Period: The first ionization enthalpy generally increases as we go across a period. When we move from left to right in period, successive electrons are added to orbitals in the same principal quantum level and the shielding of the nuclear charge by the inner core of electrons does not increase very much to compensate for the increased attraction of the electron to the nucleus. Thus, across a period, increasing nuclear charge outweighs the shielding. Consequently, the outermost electrons are held more and more tightly and the ionization enthalpy increases across a period



21. Electron Gain Enthalpy: When an electron is added to a neutral gaseous atom (X) to convert it into a negative ion, the enthalpy change accompanying the process is defined as the Electron Gain Enthalpy ($\Delta_{eg}H$). Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion as represented by equation. $X(g) + e^- \rightarrow X^-(g)$. Depending on the element, the process of adding an electron to the atom can be either endothermic or exothermic. For many elements energy is released when an electron is added to the atom and the electron gain enthalpy is negative. For example, group 17 elements (the halogens) have very high negative electron gain enthalpies because they can attain stable noble gas electronic configurations by picking up an electron. On the other hand, noble gases have large positive

electron gain enthalpies because the electron has to enter the next higher principal quantum level leading to a very unstable electronic configuration.

22. Variation in electron gain enthalpies in Group & period: The variation in electron gain enthalpies of elements is less systematic than for ionization enthalpies. As a general rule, electron gain enthalpy becomes more negative with increase in the atomic number across a period. The effective nuclear charge increases from left to right across a period and consequently it will be easier to add an electron to a smaller atom since the added electron on an average would be closer to the positively charged nucleus. We should also expect electron gain enthalpy to become less negative as we go down a group because the size of the atom increases and the added electron would be farther from the nucleus. This is generally the case. However, electron gain enthalpy of O or F is less negative than that of the succeeding element. This is because when an electron is added to O or F, the added electron goes to the smaller $n = 2$ quantum level and suffers significant repulsion from the other electrons present in this level. For the $n = 3$ quantum level (S or Cl), the added electron occupies a larger region of space and the electron-electron repulsion is much less.

23. Electronegativity: A qualitative measure of the ability of an atom in a chemical compound to attract shared electrons to itself is called electro negativity Linus Pauling, an American scientist, in 1922 assigned arbitrarily a value of 4.0 to fluorine, the element considered to have the greatest ability to attract electrons. Electronegativity generally increases across a period from left to right (say from lithium to fluorine) and decrease down a group (say from fluorine to astatine) in the periodic table.

24. Anomalous Properties of Second Period Elements: The first element of each of the groups 1 (lithium) and 2 (beryllium) and groups 13-17 (boron to fluorine) differs in many respects from the other members of their respective group. For example, lithium unlike other alkali metals, and beryllium unlike other alkaline earth metals, form compounds with pronounced covalent character; the other members of these groups predominantly form ionic compounds. In fact the behaviour of lithium and beryllium is more similar with the second element of the Group 1, 2 ,13, 14, 15, 16 ,17. following group i.e., magnesium and aluminum, respectively. This sort of similarity is commonly referred to as **diagonal relationship** in the periodic properties. The anomalous behaviour is attributed to their small size, large charge/ radius ratio and high electronegativity of the elements. In addition, the first member of group has only four valence orbitals ($2s$ and $2p$) available for bonding, whereas the second member of the groups have nine valence orbitals ($3s$, $3p$, $3d$). As a consequence of this, the maximum covalency of the first

member of each group is 4 (e.g., boron can only form $[BF_4]^-$, whereas the other members of the groups can expand their valence shell to accommodate more than four pairs of electrons e.g., aluminum forms $[AlF_6]^{3-}$). Furthermore, the first member of *p*-block elements displays greater ability to form $p\pi - p\pi$ multiple bonds to itself (e.g., C = C, C ≡ C, N = N, N ≡ N) and to other second period elements (e.g., C = O, C = N, C ≡ N, N = O) compared to subsequent members of the same group.

Unit-3

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

1. Questions based on Modern Periodic Table

1. Which important property did Mendeleev use to classify the elements in his periodic table and did he stick to that?
2. What is the basic difference in approach between the Mendeleev's Periodic Law and the Modern Periodic Law?
3. What would be the IUPAC name and symbol for the elements with atomic number 101 to 120?
4. Write a detailed note on the present form of the periodic Table (Modern Periodic Table.) Draw colourful Periodic Table.
5. (a) How is group, period and block of elements predicted.
(b) Give the electronic configuration and in terms of period group and block where would you locate the elements with Z= 17, 19, 24, 26, 29, 31, 34, 38, 40, 51, 55, 114, 117 and 120 ?
6. How would you justify the presence of 18 elements in the 5th period of the Periodic Table?
7. On the basis of quantum numbers, justify that the sixth period of the periodic table should have 32 elements.
8. .Write the general outer electronic configuration s, p, d, & f block elements.
9. Give five properties each of s, p, d, & f block elements.
10. Why do elements in the same group have similar physical and chemical properties?

2. Questions based on Atomic Radius & Ionic Radius

1. How is atomic radius expressed in terms of different types of radius?
2. How does the atomic radius vary in a period and in a group? How do you explain the variation?

3. Why atomic radius of noble gases are not considered in comparison.
4. Explain why cations are smaller and anions larger in radii than their parent atom? Or
Describe the theory associated with the radius of an atom as it (a) gains an electron
(b) Loses an electron
5. What do you understand by isoelectronic species? Name a species that will be isoelectronic with each of the following atoms or ions.(i) F^- (ii) Ar (iii) Mg^{+2} (iv) Rb^+
6. Consider the following species: N^{3-} , O^{2-} , Na^+ , Mg^{+2} , and Al^{+3}
(a)What is common in them? (b)Arrange them in the order of increasing ionic radii.
7. Arrange the following in order of increasing radii: (a) N,O,P (b) F,Cl,Br (c) I,I^+
8. Which of the following species will have the largest and the smallest size Mg , Mg^{2+} , Al , Al^{3+} .
9. A student reported the radii of Cu,Cu^+ and Cu^{+2} as 96,122 & 72 ppm respectively do you agree with results.

3. Questions based on Ionization Enthalpy its Variation and factors affecting it.

1. (a)Define Ionization enthalpy. Give its unit.
(b)Explain the term successive ionization energies.
2. How does the Ionization vary in a period and in a group? How do you explain the variation?
3. Among the second period elements the actual ionization enthalpies are in the order $Li < B < Be < C < O < N < F < Ne$
Explain why (i) Be has higher ionization enthalpy than B.
(ii)O has lower ionization enthalpy than N and F?
4. How would you explain the fact the first ionization enthalpy of sodium is lower than that of Magnesium but its second ionization enthalpy is higher than that of Magnesium?
5. What are the various factors due to which the ionization enthalpy of the main group elements tends to decrease down a group?
6. .The first ionization enthalpy values (in $KJ\ mol^{-1}$) of group 13 are:

| B | Al | Ga | In | Tl |
|-----|-----|-----|-----|-----|
| 801 | 577 | 579 | 558 | 589 |

How would you explain this deviation from the general trend?

7. (a)Arrange C,N,O and F in the decreasing order of their second ionization enthalpy and explain briefly.
(b)Explain why the first ionization enthalpy of Carbon is more than that of Boron but the reverse is true for second ionization enthalpy

8. Would you expect the first ionization enthalpy for two isotopes of the same element to be same or different? Justify your answer.

4. Questions based on electron gain enthalpy its Variation and factors affecting it

\$1. Define the term electron gain enthalpy.

\$2. How does the electron gain enthalpy in a period and in a group? How do you explain the variation?

\$3. Would you expect the second electron gain enthalpy of O as positive, more negative or less negative than the first? Justify your answer?

\$4. Which of the following pairs of elements would have a more negative electron gain enthalpy? (i) O or F (ii)F or Cl (iii) O or S. Give reason to support your answer

5. Which of the following will have the most negative electron gain enthalpy and which the least negative? P, S, Cl, F. Explain your answer.

6. In each of the following sets, arrange the elements in the increasing order of their negative electron gain enthalpies: (i)C,N,O (ii)O,N,S (iii) Cl,S,Ar (iv)F,Cl,Br

5. Miscellaneous Questions

1. Which element do you think would have been named by

(i) Lawrence Berkeley Laboratory (ii) Seaborg's group?

2. What is the significance of the terms — 'isolated gaseous atom' and 'ground state' while defining the ionization enthalpy and electron gain enthalpy?

3. Energy of an electron in the ground state of the hydrogen atom is -2.18×10^{-18} J. Calculate the ionization enthalpy of atomic hydrogen in terms of J mol^{-1} .

4. What is the difference between the terms electron gain enthalpy and electronegativity?

5. How would you react to the statement that the electronegativity of N on Pauling scale is 3.0 in all the nitrogen compounds?

6. Use the periodic table to answer the following questions.

(a) Identify an element with five electrons in the outer subshell. (b) Identify an element that would tend to lose two electrons. (c) Identify an element that would tend to gain two electrons. (d) Identify the group having metal, non-metal, liquid as well as gas at the room temperature.

7. The increasing order of reactivity among group 1 elements is Li < Na < K < Rb < Cs whereas that among group 17 elements is F > Cl > Br > I. Explain.

8. Assign the position of the element having outer electronic configuration (i) ns^2np^4 for n=3(ii)(n-1)d² ns² (iii)(n-2)f⁷ (n-1)d¹ns² for n=6 in the periodic table.

9. Predict the formulas of the stable binary compounds that would be formed by the combination of the following pairs of elements.

- (a) Lithium and oxygen (b) Magnesium and nitrogen (c) Aluminum and iodine (d) Silicon and oxygen
(e) Phosphorus and fluorine (f) Element 71 and fluorine (g) silicon and bromine (h) aluminum and sulphur.

10. Considering the elements B, Al, Mg, and K, the correct order of their metallic character is 11.

Considering the elements B, C, N, F, and Si, the correct order of their non-metallic character is:

12. Considering the elements F, Cl, O and N, the correct order of their chemical reactivity in terms of oxidizing property is:

13. Show by a chemical reaction with water that Na_2O is a basic oxide and Cl_2O_7 is an acidic oxide.

14. Considering the atomic number and position in the periodic table, arrange the following elements in the increasing order of metallic character : Si, Be, Mg, Na, P.

15. The element with atomic number 119 has not been discovered. What would be the IUPAC name and symbol of this element? Also predict the electronic configuration, group and period of this element.

16. Which element has the highest negative electron gain enthalpy, ionization enthalpy and electronegativity?

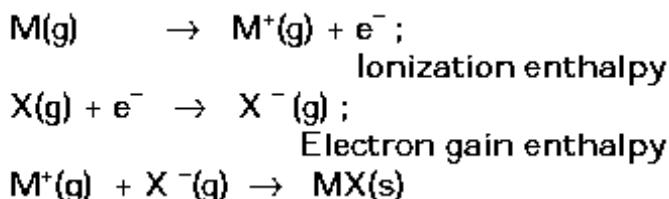
4. Chemical bonding and Molecular Structure

Some Important Points and Terms of the Chapter

1. **Lewis dot structures** are shorthand to represent the valence electrons of an atom. The structures are written as the element symbol surrounded by dots that represent the valence electrons.
2. **Covalent Bonds-** The bond formed between two atoms by mutual sharing of electrons between them so as to complete their octets or duplets. When two atoms share one electron pair they are said to be joined by a single covalent bond.e.g H₂ If two atoms share two electron pairs of electrons, the covalent bond between them is called a double bond. e.g O₂ If two atoms share three electron pairs of electrons, the covalent bond between them is called a triple bond. e.g N₂
3. **Octet Rule-** Kossel and Lewis in 1916 developed an important theory of chemical combination between atoms known as electronic theory of chemical bonding. According to this, atoms can combine either by transfer of valence electrons from one atom to another or by sharing of valence electrons in order to attain their octet. This is known as octet rule.
4. **Limitations of octet rule-**
 - a) Incomplete octet of the central atom: In some compounds the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples- LiCl ,BeCl₂ , BCl₃
 - b) Odd-electron molecules: In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, the octet rule is not satisfied for all the atoms.
 - c) The expanded octet : Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Some of examples of such compounds are: PF₅, SF₆.
 - d) This theory does not account for the shape of molecules.
5. **Electrovalent bond or Ionic Bond:** The chemical bond as result of transfer of electron from one atom(electropositive) to another atom (electronegative).Ionic bonds will be formed_more easily between elements with_comparatively low ionization enthalpies_and elements with comparatively

high negative value of electron gain enthalpy. Most ionic compounds have cations derived from metallic elements and anions from non-metallic elements.

6. Formation of Ionic Bond



7. **Bond length** is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule.
8. **Bond Angle:** It is defined as the angle between the orbital containing bonding electron pairs around the central atom in a molecule/complex ion. It gives some idea regarding the distribution of orbital around the central atom in a molecule/complex ion and hence it helps us in determining its shape
9. **Bond enthalpy:** It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. The unit of bond enthalpy is kJ mol^{-1}
10. **Bond Order :** The Bond Order is given by the number of bonds between the two atoms in a molecule. E.g.: Bond Order of $\text{O}_2 = 2$. With increase in bond order, bond enthalpy increases and bond length decreases.
11. **Resonance:** According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and the non- bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately
12. **Polarity of bonds:** In case of heteronuclear molecules like HCl, the shared pair of electron between the two atoms gets displaced more towards chlorine since the electronegativity of chlorine is far greater than that of hydrogen. The resultant covalent bond is called a polar covalent bond.
13. **Dipole moment:** As a result of polarization, the molecule possesses the dipole moment which can be defined as the product of charge and the distance between the centers of positive and negative charge. It is usually designated by a Greek letter ‘ μ ’. Mathematically, it is expressed as follows:

$$\text{Dipole moment } (\mu) = \text{charge } (Q) \times \text{distance of separation } (r)$$

14. **VSEPR Theory**

- The shape of a molecule depends upon the number of valence shell electron pairs (bonded or nonbonded) around the central atom.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- These pairs of electrons tend to occupy such positions in space that minimize repulsion and thus maximise distance between them.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.
- The repulsive interaction of electron pairs decrease in the order: Lone pair (lp) – Lone pair (lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) – Bond pair (bp)
- **Geometry of Molecules** on the basis of VSEPR Theory

| Bond pair | Lone pair | Shape | Examples |
|-----------|-----------|----------------------|-------------------------------------|
| 2 | 0 | Linear | BeCl ₂ |
| 3 | 0 | Trigonal Planar | BCl ₃ |
| 2 | 1 | Bent | SO ₂ |
| 4 | 0 | Tetrahedral | CH ₄ |
| 3 | 1 | Pyramidal | NH ₃ , PH ₃ , |
| 2 | 2 | V-shape | H ₂ O |
| 5 | 0 | Trigonal bipyramidal | PCl ₅ |
| 4 | 1 | See saw | SF ₄ |
| 3 | 2 | T-shaped | CIF ₃ , |
| 2 | 3 | Linear | XeF ₂ |
| 5 | 1 | Square pyramidal | CIF ₅ , IF ₅ |
| 4 | 2 | Square planar | XeF ₄ , |
| 6 | 1 | Distorted Octahedral | XeF ₆ |

15. Hybridization: It can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formations of new set of orbitals of equivalent energies and shape.

- **Salient Features of hybridization :**

- The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
- The hybridised orbitals are always equivalent in energy and shape.
- The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
- These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement.

16. Types of Hybridisation

- **sp hybridisation-** This type of hybridisation involves the mixing of one s and one p orbital resulting in the formation of two equivalent sp hybrid orbitals.e.g. BeCl_2
- **sp² hybridisation-** In this hybridisation there is involvement of one s and two p-orbitals in order to form there equivalent sp² hybridised orbitals. e.g. BCl_3
- **sp³ hybridisation-** When there is mixing of one s and three p-orbitals of the valence shell to form four sp³ hybrid orbitals of equivalent energies and shape. e.g. CH_4

17. Molecular orbital. It gives electron probability distribution around a group of nuclei in a molecule. They are filled in the same way as atomic orbitals. Molecular orbitals are formed by linear combination of atomic orbitals.

18. Bonding molecular orbital. A molecular orbital that is formed by addition overlap (*i.e.,* when the lobes of atomic orbitals overlap with the same sign) of two atomic orbitals is known as *bonding molecular orbital*. It is represented as

$$\Psi_{MO} = \Psi_A + \Psi_B$$
 Its energy is lower than the atomic orbitals from which it is formed. It favours bonding.

19. Anti-bonding molecular orbital. A molecular orbital that is obtained by the subtraction overlap (*i.e.,* when the lobes of atomic orbitals overlap with the opposite sign) of two atomic orbitals is know as *anti-bonding molecular orbital*. It is represented as

$$\Psi^{*}_{MO} = \Psi_A - \Psi_B$$
 Its energy is higher than the atomic orbitals from which it is formed. It does not favour bonding.

20. Bond order. It is defined as half of the difference between number of electrons in bonding and anti-bonding orbitals, i.e., $B.O. = \frac{1}{2} (N_b - N_a)$ ‘where N_b are number of electrons in bonding orbitals’ and N_a are number of electrons in anti-bonding orbitals. Bond order helps in estimating stability of atom.

21. Relationship between electronic configuration and molecular behaviour :

- (a) If N_b is greater than N_a , the molecule is stable.
- (b) The molecule is unstable if N_a is greater than N_b .
- (c) The molecule is also unstable if N_a is equal to N_b because anti-bonding effect is stronger than bonding effect.

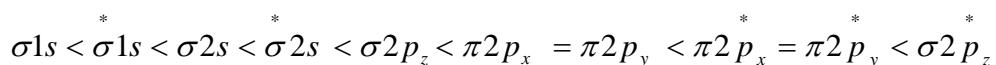
22. Sigma (σ) molecular orbitals. A molecular orbital which is formed from the overlap of two s atomic orbitals or head to head overlap of one s and p -atomic orbitals or head to head overlap of two p -atomic orbitals, is known as *sigma molecular orbital*.

23. pi (π) molecular orbitals. A molecular orbital which is formed by lateral overlap of two parallel p -orbitals is known as *pi (π) molecular orbital*.

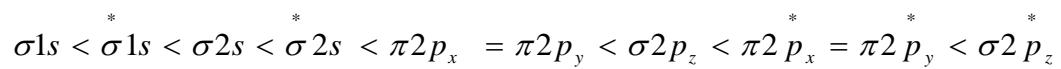
24. Conditions for the Combination of Atomic Orbitals. The linear combination of atomic orbitals takes place only if the following conditions are satisfied :

- (i) The combining atomic orbitals must have same or nearly same energy.
- (ii) The combining atomic orbitals must have the same symmetry about the molecular axis. By convention, z -axis is taken as the molecular axis.
- (iii) The combining atomic orbitals must overlap to the maximum extent. Greater the extent of overlapping, the greater will be electron density between the nuclei of a molecular orbital.

25. Energy level Diagrams for Molecular Orbitals. The increasing order of energies of various molecular orbitals for O_2 and F_2 is given below.



However, this sequence of energy levels of molecular orbitals is not correct for remaining molecules Li_2 , Be_2 , B_2 , C_2 , N_2 . For instance, it has been observed experimentally that for molecules such as B_2 , C_2 , N_2 etc., the increasing order of energies of various molecular orbitals is



The important characteristic feature of this order is that the energy of $\sigma 2p_z$ **molecular orbital is higher than that of $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals** in these molecules.

Unit-4

CHEMICAL BONDING & MOLECULAR STRUCTURE

1. Questions based on Lewis dot symbols & structures, Covalent Bond,

Formal Charge, Electrovalent Bond & octet rule

1. Write Lewis dot symbols for atoms of the following elements : Mg, Na, B, O, N, Br, Cl, F, Li, Al, Be, P, As, S, Xe, H
2. Write Lewis symbols for the following atoms and ions: S^{2-} , Al^{3+} and H^-
3. Define Covalent Bond. Explain its types with examples.
4. Draw the Lewis structures for the following molecules&ions: H_2S , $SiCl_4$, BeF_2 , CO_2^{3-} , $BeCl_2$, BCl_3 , $SiCl_4$, AsF_5 , H_2S , PH_3 , PCl_5 , SF_6 , NH_3 , SF_4 , ClF_3 , BrF_5 , XeF_4 , NO_3^-
5. Explain some compounds which are exceptions to Octet rule.
6. What is Formal Charge? Calculate the formal charge on all elements of O_3 & CO_3^{2-} .
7. Define Electrovalent Bond or Ionic Bond. Write the favorable factors for the formation of ionic bond.
8. Use Lewis symbols to show electron transfer between the following atoms to form Cations and anions: (a) K and S (b) Ca and O (c) Al and N (d) Al and O
9. (a) Define octet rule. Write its significance and limitations. (b) What is Coordinate Bond or Dative Bond.

2. Questions based on VSEPR theory, Resonance, Dipole moment,

Valence Bond Theory., hybridization of atomic orbitals

10. (a) Give the main points of VSEPR theory
- (b) Discuss the shape using the VSEPR model: H_2S , $SiCl_4$, BeF_2 , CO_2^{3-} , $BeCl_2$, BCl_3 , $SiCl_4$, AsF_5 , H_2S , PH_3 , PCl_5 , SF_6 , NH_3 , SF_4 , ClF_3 , BrF_5 , XeF_4 , NO_3^-
11. Although geometries of NH_3 and H_2O molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. Discuss.
12. Define Resonance. Explain the structure of CO_3^{2-} ion in terms of resonance.
13. Write the resonance structures for SO_3 , NO_2 and NO_3^- , CO_2

14. Explain the Dipole moment. How it is helpful in predicting polar & Non polar nature of compounds.
15. Explain why BeH₂ molecule has zero dipole moment although the B-H bonds are polar.
16. Which out of NH₃ and NF₃ has dipole moment and why?
17. Arrange the bonds in order of increasing ionic character in the molecules: LiF, K₂O, N₂, SO₂ and ClF₃.
18. Explain the formation of Hydrogen molecule on basis of Valence Bond Theory.
19. (a) Distinguish between a sigma (σ) and a pi (π) bond
(b) What is the total number of sigma and pi bonds in the following molecules?
(a) C₂H₂ (b) C₂H₄.
20. What is meant by hybridization of atomic orbitals?
21. Describe sp, sp², sp³ hybrid orbitals using suitable examples.
22. Describe the change in hybridization (if any) of the Al atom in the following reaction: AlCl₃ + Cl⁻ → AlCl₄⁻
23. Is there any change in the hybridization of B and N atoms as a result of the following reaction: BF₃ + NH₃ → F₃B.NH₃
24. Predict the hybrid state of central atom in the following compounds: H₂S, SiCl₄, BeF₂, CO₂³⁻, BeCl₂, BCl₃, SiCl₄, AsF₅, H₂S, PH₃, PCl₅, SF₆, NH₃, SF₄, ClF₃, BrF₅, XeF₄.
25. Explain the concept of hybridization in PCl₅. Why are axial bonds longer as compared to equatorial bonds in PCl₅.
26. Which hybrid orbitals are used by carbon atoms in the following molecules?
(a) CH₃-CH₃ (b) CH₃-CH=CH₂ (c) CH₃-CH₂-OH (d) CH₃-CHO (e) CH₃-COOH
(f) H₂C=CH-CH₂-C≡CH
- 3. Questions based on Atomic orbitals , Molecular orbital configuration and energy diagram, Bond order & Hydrogen bond**
27. Write the conditions for the combination of atomic orbitals.
28. Distinguish between bonding molecular orbital & anti bonding molecular orbital.
29. Write the molecular orbital configuration and energy diagram for (i) O₂⁺, O₂, O₂⁻, O₂²⁻ (ii) N₂, N₂⁺, N₂⁻ (iii) Be₂, H₂, C₂
30. Draw the energy diagram for H₂, Be₂, N₂ & O₂.
31. a) What is meant by the term bond order. Write the significance of bond order

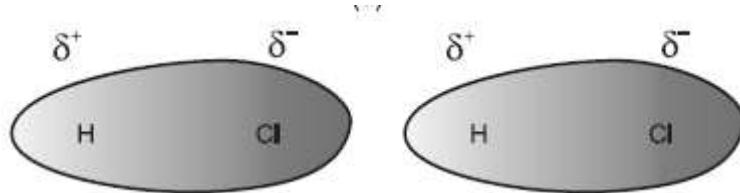
- (b) Compare the relative Stability of the following species and indicate their magnetic properties. (i) O_2^+ , O_2 , O_2^- , O_2^{2-} (ii) N_2 , N_2^+ , N_2^-
32. Use the molecular orbital theory to explain why Be_2 molecule does not exist.
- 33.(a) Define hydrogen bond .Explain its types with suitable examples.
- (b) Is it weaker or stronger than the van der Waals forces?



5. States of Matter

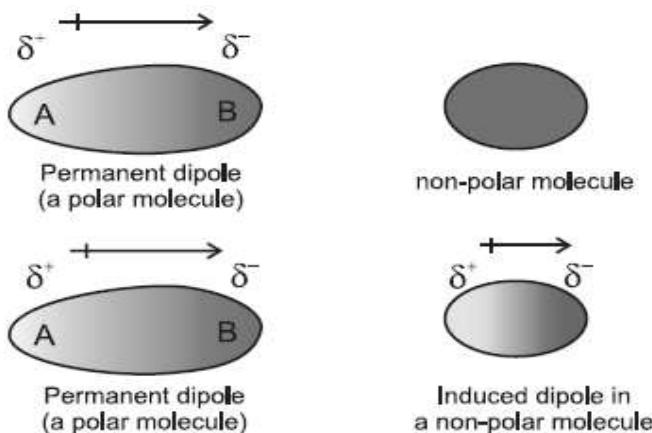
Some Important Points and Terms of the Chapter

1. **Intermolecular forces** are the forces of attraction and repulsion between interacting particles (atoms and molecules). This term does not include the electrostatic forces that exist between the two oppositely charged ions and the forces that hold atoms of a molecule together i.e., covalent bonds. Attractive intermolecular forces are known as van der Waals forces, in honour of Dutch scientist Johannes van der Waals (1837-1923).
2. **Dipole - Dipole Forces:** Dipole-dipole forces act between the molecules possessing permanent dipole. Ends of the dipoles possess “partial charges” and these charges are shown by Greek letter *delta* (δ)



3. **Dipole -Induced Dipole Forces:** This type of attractive forces operate between the polar molecules having permanent dipole and the molecules lacking permanent dipole. Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electronic cloud. Thus an

induced dipole is developed in the other molecule



4. **Dispersion Forces or London Forces:** Atoms and nonpolar molecules are electrically symmetrical and have no dipole moment because their electronic charge cloud is symmetrically distributed. But a dipole may develop momentarily even in such atoms and molecules. This can be understood as follows. Suppose we have two atoms 'A' and 'B' in the close vicinity of each other (Fig. 5.1a NCERT page 133). It may so happen that momentarily electronic charge distribution in one of the atoms, say 'A', becomes unsymmetrical *i.e.*, the charge cloud is more on one side than the other (Fig. 5.1 b and c NCERT page 133). This results in the development of instantaneous dipole on the atom 'A' for a very short time. This instantaneous or transient dipole distorts the electron density of the other atom 'B', which is close to it and as a consequence a dipole is induced in the atom 'B'. The temporary dipoles of atom 'A' and 'B' attract each other. Similarly temporary dipoles are induced in molecules also. This force of attraction was first proposed by the German physicist Fritz London, and for this reason force of attraction between two temporary dipoles is known as **London force**. Another name for this force is **dispersion force**.

5. **Hydrogen bond:** Hydrogen bond is represented by a dotted line (---) while a solid line represents the covalent bond. Thus, hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule this is special case of dipole-dipole interaction..

6. **Boyle's Law (Pressure – Volume Relationship):** At constant temperature, the pressure of a fixed amount (i.e., number of moles n) of gas varies inversely with its volume. This is known as Boyle's law.

$$p \propto \frac{1}{V} \text{ (at constant T & V)} \quad \text{i.e.} \quad p = K_1 \frac{1}{V} \quad pV = K_1 \quad p_1V_1 = p_2V_2$$

$$\boxed{\frac{p_1}{V_1} = \frac{p_2}{V_2}}$$

7. **Charles Law (Temperature – Volume Relationship):** It states that pressure remaining constant, the volume of a fixed mass of a gas is directly proportional to its absolute temperature.i.e. $V \propto T$ (at constant P & V)

$$V = K_2 T \quad \frac{V}{T} = K_2 \quad \boxed{\frac{V_1}{T_1} = \frac{V_2}{T_2}}$$

8. **Gay Lussac's Law (Pressure-Temperature Relationship):** It states that at constant volume, pressure of a fixed amount of a gas varies directly with the temperature. Mathematically, . $P \propto T$ (at constant V & n)

$$p = K_3 T \quad \boxed{\frac{P}{T} = K_3}$$

9. **Avogadro Law (Volume – Amount Relationship):** It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules. i.e. $V \propto n$ i.e. $\boxed{V = K_4 n}$. Since volume of a gas is directly proportional to the number of moles; one mole of each gas at standard temperature and pressure (STP)* will have same volume. Standard temperature and pressure means 273.15 K (0°C) temperature and 1 bar (i.e., exactly 10^5 pascal) pressure

10. **Ideal gas:** A gas that follows Boyle's law, Charles' law and Avogadro law strictly.

11. **Ideal Gas Equation:** $\boxed{pV = n RT}$

12. **Universal Gas Constant :**R is called gas constant. It is same for all gases. $R= 8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} = 8.314 \times 10^{-2} \text{ bar L K}^{-1} \text{ mol}^{-1} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

13. **Equation of state.** $\boxed{\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}}$

14. Density and Molar Mass of a Gaseous Substance:

$$M = \frac{dRT}{P}$$

15. Dalton's Law of Partial Pressures: It states that the total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases i.e., the pressures which these gases would exert if they were enclosed separately in the same volume and under the same conditions of temperature. In a mixture of gases, the pressure exerted by the individual gas is called partial pressure. Mathematically,

$$p_{\text{Total}} = p_1 + p_2 + p_3 + \dots \quad (\text{at constant } T, V)$$

where p_{Total} is the total pressure exerted by the mixture of gases and p_1, p_2, p_3 etc. are partial pressures of gases.

16. KINETIC MOLECULAR THEORY OF GASES:

- Gases consist of large number of identical particles (atoms or molecules) that are so small and so far apart on the average that the actual volume of the molecules is negligible in comparison to the empty space between them. They are considered as point masses. This assumption explains the great compressibility of gases.
- There is no force of attraction between the particles of a gas at ordinary temperature and pressure. The support for this assumption comes from the fact that gases expand and occupy all the space available to them.
- Particles of a gas are always in constant and random motion. If the particles were at rest and occupied fixed positions, then a gas would have had a fixed shape which is not observed.
- Particles of a gas move in all possible directions in straight lines. During their random motion, they collide with each other and with the walls of the container. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container.

- Collisions of gas molecules are perfectly elastic. This means that total energy of molecules before and after the collision remains same.

17. Behaviour Of Real Gases: Deviation From Ideal Gas: Real gases show deviations from ideal gas law (a) **Pressure correction:** pressure exerted by the gas is lower than the pressure exerted by the ideal gas.

$$P_{\text{ideal}} = P_{\text{real}} + \frac{an^2}{V^2}$$

observed correction
pressure term

Here, a is a constant.

(b) **Volume Correction:** ($V-nb$) where nb is approximately the total volume occupied by the molecules themselves. Here, b is a constant.

18. Van der Waals equation.

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

Constants a and b are called van der Waals constants

19. Significance of Vander wall parameter: Vander wall parameter a is the measure of intermolecular forces while b is the measure of effective size of gaseous molecules Unit of a = bar L³ mol⁻² Unit of b = L mol⁻¹

20. The deviation from ideal behaviour can be measured in terms of **compressibility factor Z**, which is the ratio of product pV and nRT .

Mathematically $Z = \frac{pV}{nRT}$

21. The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called Boyle temperature or **Boyle point**.

22. **Critical temperature (T_C)** of a gas is highest temperature at which liquifaction of the gas first occurs. Liquifaction of so called permanent gase Volume of one mole of the gas at critical temperature is called **critical volume (V_C)** and pressure at this temperature is called **critical pressure (p_C)**. The critical temperature, pressure and volume are called critical constants.

23. **Surface tension** is defined as the force acting per unit length perpendicular to the line drawn on the surface of liquid. It is denoted by Greek letter γ . It has dimensions of kg s^{-2} and in SI unit it is expressed as N m^{-1} .
24. **Viscosity** is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows. Strong intermolecular forces between molecules hold them together and resist movement of layers past one another. Greater the viscosity, the more slowly the liquid flows. Viscosity of liquids decreases as the temperature rises because at high temperature molecules have high kinetic energy and can overcome the intermolecular forces to slip past one another between the layers.
25. **Viscosity coefficient** is the force when velocity gradient is unity and the area of contact is unit area. Thus ' η ' is measure of viscosity. SI unit of viscosity coefficient is 1 newton second per square metre (N s m^{-2}) = pascal second ($\text{Pa s} = \text{1kg m}^{-1}\text{s}^{-1}$).

Unit-5

STATES OF MATTER

1. Questions based on Intermolecular forces ,Boyle's Law, Charles's Law, Gay Lussac's Law, Avogadro's Law

1. What are Intermolecular forces? Explain its different types with suitable example
2. State Boyle's Law. Give its mathematical Expression & graphical representation.
3. A balloon is filled with hydrogen at room temperature. It will burst if pressure exceeds 0.2 bar. If at 1 bar pressure the gas occupies 2.27 L volume, up to what volume can the balloon be expanded?
4. What will be the minimum pressure required to compress 500 dm³ of air at 1 bar to 200 dm³ at 30°C?
5. A vessel of 120 mL capacity contains a certain amount of gas at 35 °C and 1.2 bar pressure. The gas is transferred to another vessel of volume 180 mL at 35 °C. What would be its pressure?
6. State Charles's Law. Give its mathematical Expression & graphical representation.
7. On a ship sailing in pacific ocean where temperature is 23.4 °C , a balloon is filled with 2 L air. What will be the volume of the balloon when the ship reaches Indian ocean, where temperature is 26.1°C ?
8. A student forgot to add the reaction mixture to the round bottomed flask at 27 °C but instead he/she placed the flask on the flame. After a lapse of time, he realized his mistake, and using a pyrometer he found the temperature of the flask was 477 °C. What fraction of air would have been expelled out?
9. . State Gay Lussac's Law. Give its mathematical Expression & graphical representation.
10. State Avogadro's Law. Give its mathematical Expression.

ANSWER

3. A balloon is filled with hydrogen at room temperature. It will burst if pressure exceeds 0.2 bar. If at 1 bar pressure the gas occupies 2.27 L volume, up to what volume can the balloon be expanded?

Ans:

$$P_1V_1=P_2V_2$$

$$1 \times 2.27 = 0.2 \times V_2$$

$$V_2 = 2.27 / 0.2 = 11.35 \text{ L}$$

4. What will be the minimum pressure required to compress 500 dm³ of air at 1 bar to 200 dm³ at 30°C?

$$\text{Ans: } P_1V_1=P_2V_2$$

$$1 \times 500 = P_2 \times 200$$

$$P_2 = 500 / 200 = 2.5 \text{ bar}$$

5. A vessel of 120 mL capacity contains a certain amount of gas at 35 °C and 1.2 bar pressure. The gas is transferred to another vessel of volume 180 mL at 35 °C. What would be its pressure?

$$\text{Ans: } P_1V_1=P_2V_2$$

$$1.2 \times 120 = P_2 \times 180$$

$$P_2 = 0.8 \text{ bar}$$

6.

7. On a ship sailing in pacific ocean where temperature is 23.4 °C , a balloon is filled with 2 L air. What will be the volume of the balloon when the ship reaches Indian ocean, where temperature is 26.1°C ?

$$\text{Ans: } V_1/T_1 = V_2/T_2$$

$$2 / 296.4 = V_2 / 299.1$$

$$V_2 = 2.018 \text{ L}$$

8. A student forgot to add the reaction mixture to the round bottomed flask at 27 °C but instead he/she placed the flask on the flame. After a lapse of time, he

realized his mistake, and using a pyrometer he found the temperature of the flask was 477 °C. What fraction of air would have been expelled out?

Ans: $V_1/T_1 = V_2/T_2$

$$V_1/300 = V_1 + x/750$$

$$750/300 = (V_1 + x)/x$$

$$2.5 = (V_1/x) + 1$$

$$1.5 = V_1/x$$

$$x/V_1 = 0.67$$

$$x = 0.67V_1$$

The amount of air expelled out is 0.67 times the volume of the flask
0.67/1.67 = 0.4011 fraction of air is expelled.

2. Questions based on Ideal gas equation., combined gas law equation,Dalton's Law of Partial Pressures

9. Derive Ideal gas equation. Give combined gas law equation.
10. Using the Ideal gas equation Show that the density of the gas is proportional to the gas pressure p.
11. At 25°C and 760 mm of Hg pressure a gas occupies 600 mL volume. What will be its pressure at a height where temperature is 10°C and volume of the gas is
12. At 0°C, the density of a certain oxide of a gas at 2 bar is same as that of dinitrogen at 5 bar. What is the molecular mass of the oxide?
13. . Pressure of 1 g of an ideal gas A at 27 °C is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask at same temperature the pressure becomes 3 bar. Find a relationship between their molecular masses. 640 mL.
14. What will be the pressure exerted by a mixture of 3.2 g of methane and 4.4 g of carbon dioxide contained in a 9 dm³ flask at 27 °C ?

15. What will be the pressure of the gaseous mixture when 0.5 L of H_2 at 0.8 bar and 2.0 L of dioxygen at 0.7 bar are introduced in a 1L vessel at 27°C?
16. Density of a gas is found to be 5.46 g/dm³ at 27 °C at 2 bar pressure. What will be its density at STP?
- 17.. 34.05 mL of phosphorus vapour weighs 0.0625 g at 546 °C and 0.1 bar pressure. What is the molar mass of phosphorus?
18. Calculate the temperature of 4.0 mol of a gas occupying 5 dm³ at 3.32 bar. ($R = 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$).
19. Calculate the total pressure in a mixture of 8 g of dioxygen and 4 g of dihydrogen confined in a vessel of 1 dm³ at 27°C. $R = 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$.
20. Calculate the volume occupied by 8.8 g of CO_2 at 31.1°C and 1 bar pressure. $R = 0.083 \text{ bar L K}^{-1} \text{ mol}^{-1}$.
21. 2.9 g of a gas at 95 °C occupied the same volume as 0.184 g of dihydrogen at 17 °C, at the same pressure. What is the molar mass of the gas?
22. A mixture of dihydrogen and dioxygen at one bar pressure contains 20% by weight of dihydrogen. Calculate the partial pressure of dihydrogen.
23. . State Dalton's Law of Partial Pressures. Express partial pressure in terms of mole fraction.

ANSWER

11. At 25°C and 760 mm of Hg pressure a gas occupies 600 mL volume. What will be its pressure at a height where temperature is 10°C and volume of the gas is 640m L

$$\text{Ans } P_1V_1/T_1 = P_2V_2/T_2$$

$$760 \times 600/298 = P_2 \times 640/283$$

$$P_2 = 760 \times 600 \times 283 / 298 \times 640 = 676.6 \text{ mm of Hg}$$

12. At 0°C, the density of a certain oxide of a gas at 2 bar is same as that of dinitrogen at 5 bar. What is the molecular mass of the oxide?

$$\text{Ans: PV=nRT}$$

$$PV = (m/M)RT$$

$$d = M_1 P_1 / RT = M_2 P_2 / RT$$

$$M_1 P_1 = M_2 P_2$$

$$M_1 = 28 \times 5 / 2 = 70$$

13. Pressure of 1 g of an ideal gas A at 27 °C is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask at same temperature the pressure becomes 3 bar. Find a relationship between their molecular masses.

Ans: $n_a = 1/M_a$, $n_b = 2/M_b$

$$PV = nRT$$

$$2V = 1/M_a RT \rightarrow V = (1/M_a)RT/2$$

$$3V = (2/M_b + 1/M_a)RT \rightarrow V = (2/M_b + 1/M_a)RT/3$$

$$(1/M_a)RT/2 = (2/M_b + 1/M_a)RT/3$$

$$(1/M_a) = 2/3 (2/M_b + 1/M_a)$$

$$(1/3M_a) = 4/3M_b$$

$$\rightarrow 1/M_a = 4/M_b \rightarrow M_b = 4M_a$$

14. What will be the pressure exerted by a mixture of 3.2 g of methane and 4.4 g of carbon dioxide contained in a 9 dm³ flask at 27 °C ?

Ans: $PV = nRT$

$$n = (3.2/16 + 4.4/44) = 0.3$$

$$P = 0.3 \text{ mole} \times 0.083 \text{ bar dm}^3/\text{mole} \times 300\text{K} / 9\text{dm}^3$$

$$P = 0.83 \text{ bar}$$

15. What will be the pressure of the gaseous mixture when 0.5 L of H₂ at 0.8 bar and 2.0 L of dioxygen at 0.7 bar are introduced in a 1L vessel at 27°C?

Ans: $PV = nRT$

$$P_1 V_1 = P_x V_2 \rightarrow 0.5 \times 0.8 = P_x \times 1 \rightarrow \text{pressure of H}_2 \text{ in the flask} = P_x = 0.40 \text{ bar}$$

$$P_1 V_1 = P_x V_2 \rightarrow 0.7 \times 2 = P_x \times 1 \rightarrow \text{pressure of oxygen in the flask} = 1.4 \text{ bar}$$

$$\text{Pressure of the gaseous mixture} = 1.4 + 0.4 = 1.8 \text{ bar.}$$

16. Density of a gas is found to be 5.46 g/dm³ at 27 °C at 2 bar pressure. What will be its density at STP?

Ans: $d = PM/RT \rightarrow M = dRT/P = 5.46 \times 0.083 \times 300 / 2 = 70$

$$d = (1.013 \times 70) / (0.083 \times 273) = 3.13 \text{ g/dm}^3$$

17. 34.05 mL of phosphorus vapour weighs 0.0625 g at 546 °C and 0.1 bar pressure. What is the molar mass of phosphorus?

Ans: $d = (0.0625 \times 1000) / 34.05 \text{ g/L}$

$$M = dRT/P = 1.836 \times 0.08314 \times 819 / 0.1 = 1250$$

18. Calculate the temperature of 4.0 mol of a gas occupying 5 dm³ at 3.32 bar. ($R = 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$).

Ans: $PV = nRT$

$$T = PV/nR = (3.32 \times 5) / (4 \times 0.083) = 50 \text{ K}$$

19. Calculate the total pressure in a mixture of 8 g of dioxygen and 4 g of dihydrogen confined in a vessel of 1 dm³ at 27°C. $R = 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$.

$$n = n_{O_2} + n_{H_2} = 8/32 + 4/2 = 0.25 + 2 = 2.25 \text{ moles}$$

$$PV = nRT; P = nRT/V = 2.25 \times 0.083 \times 300 / 1 = 56.025 \text{ bar}$$

20. Calculate the volume occupied by 8.8 g of CO₂ at 31.1°C and 1 bar pressure.

$$R = 0.083 \text{ bar L K}^{-1} \text{ mol}^{-1}$$

Ans: $PV = nRT; n = 8.8 / 44 = 0.2$

$$V = nRT/P = 0.2 \times 0.083 \times 304.1 / 1 = 5.05 \text{ L}$$

21. 2.9 g of a gas at 95 °C occupied the same volume as 0.184 g of dihydrogen at 17 °C, at the same pressure. What is the molar mass of the gas?

Ans: $PV = nRT$

$$V = nRT/P = (0.184/2) \times R \times 290 / P = (2.9/M) \times R \times 368 / P$$

$$0.092 \times 290 = 368 \times 2.9 / M$$

$$M = 368 \times 2.9 / 0.092 \times 290 = 40$$

22. A mixture of dihydrogen and dioxygen at one bar pressure contains 20% by weight of dihydrogen. Calculate the partial pressure of dihydrogen.

Ans: let 20g H₂ + 80g O₂

$$n = 20/2 + 80/32 = 10 + 2.5 = 12.5$$

$$\text{Mole fraction of H}_2 = 10/12.5 = 0.8$$

$$p_{H_2} = 0.8 \times P$$

3. Questions based on Kinetic molecular theory of gases, Vander Waal modified the ideal gas equation, Surface Tension & Viscosity

27. Critical temperature for CO₂ and CH₄ are 31.0°C and – 81.9°C respectively.

Which of these has stronger intermolecular forces and why?

Ans: CO₂ has stronger forces of attraction because it can be liquefied more easily ie at a higher temperature.

6. Thermodynamics

Some Important Points and Terms of the Chapter

1. **System and the Surroundings:** A system in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the surroundings. The surroundings include everything other than the system. System and the surroundings together constitute the universe. The wall that separates the system from the surroundings is called **boundary**
2. **Types of the System:**
 - **Open System:** In an open system, there is exchange of energy and matter between system and surroundings.
 - **Closed System** In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings.
 - **Isolated system** :In an isolated system, there is no exchange of energy or matter between the system and the surroundings
3. **State of a System:** The state of a system means the condition of the system which is described in terms of certain observable properties such as temp(T), pressure(p), volume (v), etc. of the systems. These properties of a system are called state variables.
4. **State Functions:** A physical quantity is solid to be state functions of its value depends only upon the state of the system and does not depend upon the path by which this state has been attained.
5. **Internal Energy:** a quantity which represents the total energy of the system. It may be chemical, electrical and mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the internal energy, U of the system.

6. **Isothermal Process:** When a process is carried out in such a manner that the temp remains constant throughout this process, it is called an isothermal process.
7. **Adiabatic Process:** Process is carried out in such a manner that no heat can flow from the system to the surrounding or vice versa.
8. **Isochoric Process:** Process during which the volume of the system is kept constant.
9. **Isobaric Process:** Process during which the pressure of the system is kept constant. .
10. The positive sign expresses that Work (w_{ad}) is positive when work is done **on** the system. Similarly, if the work is done **by** the system, w_{ad} will be negative.
11. The q is positive, when heat is transferred from the surroundings to the system and q is negative when heat is transferred from system to the surroundings.
12. **First law of Thermodynamics:** Statement: Energy can neither be created nor destroyed, however it may be converted from one form to another.

or

The total energy of the universe remains constant although it may undergo transformation from one to another.

Mathematical expression = $\Delta U = q + w$
13. A process or change is said to be **reversible**, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. A **reversible process** proceeds infinitely slowly by a series of equilibrium states such that system and the surroundings are always in near equilibrium with each other. Processes other than reversible processes are known as **irreversible processes**.
14. **Difference between Reversible Process & Irreversible Process**

| Reversible Process | Irreversible Process |
|---|---|
| <p>1. The process is carried out infinitesimally slowly</p> <p>2. At any stage, the equilibrium is not disturbed</p> <p>3. It takes infinite time for completion.</p> <p>4. Work obtained in this process is maximum.</p> | <p>1. It is carried out rapidly</p> <p>2. Equilibrium may exist only after the completion of the process.</p> <p>3. It takes a finite time for completion.</p> <p>4. Work obtained in this process is not maximum</p> |

15. **Enthalpy, H :** The enthalpy H [Greek word *enthalpien*, heat content] is defined as : $H = U + pV$ For finite changes at constant pressure, we can write above equation as $\Delta H = \Delta U + \Delta pV$ Since p is constant, we can write $\Delta H = \Delta U + p\Delta V$ since $p\Delta V = \Delta n_g RT$,therefore $\boxed{\Delta H = \Delta U + \Delta n g RT}$

16. **Extensive property:** An extensive property is a property whose value depends on the quantity or size of matter present in the system. For example, mass, volume, internal energy, enthalpy, heat capacity, etc. are extensive properties.

17. **Intensive property:** Those properties which do not depend on the quantity or size of matter present are known as intensive properties. For example temperature, density, pressure etc. are intensive properties.

18. **Specific heat capacity** is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree celsius (or one kelvin). For finding out the heat, q , required to raise the temperatures of a sample, we multiply the specific heat of the substance, c , by the mass m , and temperatures change, ΔT as $q = c \times m \times \Delta T = C \Delta T$.

19. **Relationship between C_p and C_v for an ideal gas:** $C_p - C_v = R$

20. **Bomb calorimeter:** For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter . Here, a steel vessel (the bomb)

is immersed in a water bath. The whole device is called calorimeter. The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings. A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb calorimeter is sealed, its volume does not change i.e., the energy changes associated with reactions are measured at constant volume. Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter. Even for reactions involving gases, there is no work done as $\Delta V = 0$. Temperature change of the calorimeter produced by the completed reaction is then converted to qV , by using the known heat capacity of the calorimeter with the help of equation (18).

21. **Enthalpy Change of a reaction:** The enthalpy change accompanying a reaction is called the reaction enthalpy. The enthalpy change of a chemical reaction is given by the symbol Δ_rH .

$\Delta_rH = (\text{sum of enthalpies of products}) - (\text{sum of enthalpies of reactants})$.

$$\boxed{\Delta_rH = \sum a_i H_{\text{Products}} - \sum b_i H_{\text{Reactants}}}$$

22. The **standard enthalpy of reaction** is the enthalpy change for a reaction when all the participating substances are in their standard states. The standard state of a substance at a specified temperature is its pure form at 1 bar. Standard conditions are denoted by adding the superscript $^\circ$ to the symbol ΔH , e.g., ΔH°

23. The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called **standard enthalpy of fusion or molar enthalpy of fusion**, $\Delta_{fus}H^\circ$. e.g. $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l}); \Delta_{fus}H^\circ = 6.00 \text{ kJ mol}^{-1}$.

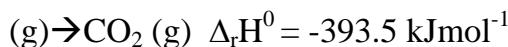
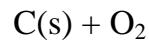
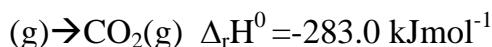
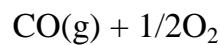
24. Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1bar) is called its **standard enthalpy of vaporization or molar enthalpy of vaporization**, $\Delta_{vap}H^\circ$. e.g. $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g}); \Delta_{vap}H^\circ = 40.79 \text{ kJ mol}^{-1}$

25. **Standard enthalpy of sublimation**, $\Delta_{sub}H^0$ is the change in enthalpy when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1bar). Sublimation is direct conversion of a solid into its vapour. Solid CO₂ (dry ice) sublimes at 195K with $\Delta_{sub}H^0=25.2 \text{ kJ mol}^{-1}$; naphthalene sublimes slowly and for this $\Delta_{sub}H^0=73.0 \text{ kJ mol}^{-1}$
26. .The **standard enthalpy change for the formation** of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. Its symbol is Δ_fH^0 .
- 27..**Standard enthalpy of combustion** is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the **reactants and products** being in their standard states at the specified temperature.
28. **Enthalpy of atomization (symbol: Δ_aH^0)**: It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase. In case of diatomic molecules, like dihydrogen the enthalpy of atomization is also the bond dissociation enthalpy. In some cases, the enthalpy of atomization is same as the enthalpy of sublimation.
29. **Bond Enthalpy (symbol: $\Delta_{bond}H^0$):**
- $$\Delta_rH = \sum \text{bondenthalpies}_{\text{reactants}} - \sum \text{bondenthalpies}_{\text{products}}$$
30. **Enthalpy of Solution (symbol : $\Delta_{sol}H^0$)**: Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible.
31. **Lattice Enthalpy** The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

32. Hess's Law: Enthalpy change for a reaction is the same whether it occurs in one step or in a series of steps. This may be stated as follows in the form of: If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature. Δ_rH^0

$$=\Delta_rH_1+\Delta_rH_2+\Delta_rH_3$$

For example: C(s) +



33. Spontaneous Process: A process which occurs by itself i.e. Without the intervention of an outside agency.

34. Non Spontaneous Process: A process which can neither take place by itself nor by initiation is called a non spontaneous process.

35. Driving Force: The force which is responsible for spontaneity of a process is called the driving force.

36. Entropy(S): Entropy is a measure of randomness or disorder of the system.

37. Entropy change (ΔS): It is defined as the amount of heat (q) observed isothermally and reversibly divided by the absolute temp(T) at which the heat is absorbed.

$$\Delta S = \frac{q}{T}$$

38. Entropy of fusion : $\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_m}$

Where, ΔH_{fusion} = Entropy of fusion per mole

T_m = Melting point

$$\Delta S_{\text{VAP}} = \frac{\Delta H_{\text{VAP}}}{T_b}$$

ΔH_{VAP} = Entropy of vaporization per mole

T_b = Boiling point

39. Second Law Of Thermodynamics

The entropy of universe is continuously increasing due to spontaneous process taking place in it.

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$$

$$\text{i.e. } \Delta S_{\text{total}} > 0$$

40. **Gibbs Free Energy (G)** : It is defined as max^m amount of energy available to a system during the process that can be converted into useful work. It is a measure of capacity to do useful work.

$$G = H - TS$$

this equation is also known as Gibb's Helmholtz equation

G is a state function. ΔG is change in free energy.

$$\Delta G = \Delta H - T\Delta S$$

41. **If ΔG is negative, process is spontaneous** when $\Delta G=0$, the process is in equilibrium if ΔG is positive, the process does not take place.
42. **Standard Free Energy Change (ΔG°)** : It is defined as free energy change measured at 298 K and 1 atm Pressure.
43. **Standard Free energy of formation:** ($\Delta_f G^{\circ}$) It is free energy change when 1 mole of compound is formed from its constituting elements in their standard state.

$$\Delta_r G^{\circ} = \sum v_p \Delta_f G^{\circ}(\text{products}) - \sum v_R \Delta_f G^{\circ}(\text{reactants})$$

44. Gibbs Energy Change and Work

In case of galvanic cell, Gibbs energy change $\Delta_r G$, is related to the electrical work done by the cell.

Thus $\boxed{\Delta_r G = -nFE_{\text{cell}}}$

If reactants and products are in their standard states

$$\Delta_r G^{\circ} = -nFE^{\circ}_{\text{cell}}, \text{ Here } E^{\circ}_{\text{cell}} \text{ is the standard cell potential.}$$

45. Gibbs Energy Change and Equilibrium Constant

$$\Delta_r G^{\circ} = -RT \ln K$$

$$\Delta_r G^{\circ} = -2.303RT \log K$$

Some Important Formulas(Thermodynamics)

- $\Delta U = q + w$

- $\Delta H = \Delta U + p\Delta V$

- $\Delta H = \Delta U + \Delta n g RT$

- $C_p - C_v = R$

- $\Delta_r H = \sum a_i H_{\text{Products}} - \sum b_i H_{\text{Reactants}}$

- $\Delta_r H = \sum \text{bond enthalpies}_{\text{reactants}} - \sum \text{bond enthalpies}_{\text{products}}$

- $\Delta_r H^0 = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3$

- $\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_m}$

- $\Delta G = \Delta H - T\Delta S$

- $\Delta_r G^\circ = \sum v_p \Delta_f G^\circ(\text{products}) - \sum v_R \Delta_f G^\circ(\text{reactants})$

- $\Delta_r G = -nFE_{\text{cell}}$

- $\Delta_r G = -2.303RT \log K$

Unit-6
THERMODYAMICS

1. Questions based on system, different types of system

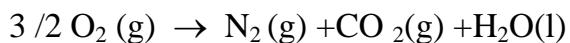
surroundings, First law of thermodynamics, internal energy

1. Define the term system and surroundings. Explain the different types of system.
2. Explain the terms: state variables, adiabatic process, work, heat & internal energy.
3. Define First law of thermodynamics. Give its mathematical expression.
4. (a) In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process? (b) Calculate the internal energy change when the system absorbs 5 KJ of heat and 1KJ of work
5. Express the change in internal energy of a system when(i) No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have?(ii) No work is done on the system, but q amount of heat is taken out from the system and given to the surroundings. What type of wall does the system have?(iii) w amount of work is done by the system and q amount of heat is Supplied to the system. What type of system would it be?

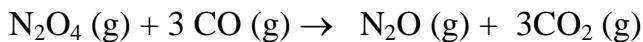
2. Questions based on system Enthalpy & its types.

6. Explain the term Enthalpy. Give its mathematical expression.
7. If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1bar and 100°C is 41kJ mol⁻¹. Calculate the internal energy change, when (i) 1 mol of water is vaporized at 1 bar pressure and 100°C. (ii) 1 mol of water is converted into ice.

8. The reaction of cyanamide, NH_2CN (s), with Dioxygen was carried out in a bomb calorimeter, and ΔU was found to be -742.7 KJ/mol at 298K. Calculate Enthalpy change for the reaction at 298K



9. Enthalpies of formation of CO (g), CO_2 (g), N_2O (g) and N_2O_4 (g) are -110, -393, 81 and 9.7 KJ/mol respectively. Find the value of $\Delta_r\text{H}$ for the reaction;



10. Given: $\text{N}_2 (\text{g}) + 3\text{H}_2 (\text{g}) \rightarrow 2\text{NH}_3 (\text{g}) ; \Delta_r\text{H}^0 = -92.4 \text{ KJ/mol}$. Calculate $\Delta_f \text{H}^0 \text{NH}_3 (\text{g})$.

11. The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, $-890.3 \text{ kJ mol}^{-1}$ $-393.5 \text{ kJ mol}^{-1}$, and $-285.8 \text{ kJ mol}^{-1}$ respectively. Calculate the Enthalpy of formation of CH_4 (g).

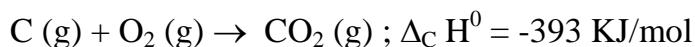
12. For the process to occur under adiabatic conditions, the correct condition is (i)
(ii) $\Delta p = 0$ (iii) $q = 0$ (iv) $w = 0$

13.. What is the enthalpies of all elements in their standard states.

14. Enthalpy of combustion of carbon to CO_2 is $-393.5 \text{ kJ mol}^{-1}$. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.

15. The combustion of 1 mol of benzene takes place at 298K .After combustion CO_2 and H_2O are formed and 3267KJ/mol of heat is liberated .calculate $\Delta_f \text{H}^0$ (C_6H_6) Given: $\Delta_f \text{H}^0 = -286 \text{ KJ/mol}$, $\Delta_f \text{H}^0 = -393 \text{ KJ/mol}$

16. Calculate the standard enthalpy of formation of CH_3OH (l) from the following data:
 $\text{CH}_3\text{OH} (\text{l}) + 3/2 \text{O}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{l}) ; \Delta_r\text{H}^0 = -726 \text{ KJ/mol}$



17. Calculate the enthalpy change for the process :

$\text{CCl}_4 (\text{g}) \rightarrow \text{C} (\text{g}) + 4\text{Cl} (\text{g})$ and calculate the bond enthalpy of C-Cl in CCl_4 (g)

$$\Delta_{\text{vap}} \text{H}^0 (\text{CCl}_4) = 30.5 \text{ KJ/mol}, \Delta_f \text{H}^0 (\text{CCl}_4) = -135.5 \text{ KJ/mol}$$

$$\Delta_a \text{H}^0 (\text{C}) = 715 \text{ KJ/mol} \quad \Delta_a \text{H}^0 (\text{Cl}_2) = 242 \text{ KJ/mol}$$

18. Define the Extensive, intensive properties & Heat capacity.

- 19(a) Give the relationship between C_p and C_v .
- (b) Write a note on Bomb Calorimeter.
20. Explain the following terms with suitable examples: (a) Standard enthalpy of reaction (b) standard enthalpy of formation (c) enthalpy of fusion (d) enthalpy of vaporization (e) enthalpy of Sublimation (f) enthalpy of Combustion (g) enthalpy of Hydration (h) enthalpy of Atomization (i) Bond enthalpy

3. Questions based on Hess's law of constant heat summation, Born Haber cycle, Entropy, Gibbs Energy

21. Explain Hess's law of constant heat summation with an example.
22. Explain Born Haber cycle & lattice enthalpy.
23. Define Entropy. Give mathematical expressions related to it.
24. Predict in which of the following, entropy increases/decreases:
- (i) A liquid crystallizes into a solid.
 - (ii) Temperature of a crystalline solid is raised from 0 K to 115 K.
 - (iii) $2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
 - (iv) $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$
25. Define Gibbs Energy. Give its mathematical expression. What is Gibb's energy criteria of Spontaneity.
26. For the reaction at 298K, $2\text{A} + \text{B} \rightarrow \text{C}$, $\Delta H = 400 \text{ KJ/mol}$ and $\Delta S = 0.2 \text{ KJ/mol K}$ At what temperature will the reaction become spontaneous?
27. For the reaction, $2\text{Cl}(\text{g}) \rightarrow \text{Cl}_2(\text{g})$, What are the signs of ΔH and ΔS ?
28. For the reaction: $2\text{A}(\text{g}) + \text{B}(\text{g}) \rightarrow 2\text{D}(\text{g})$, $\Delta U^0 = -10.5 \text{ KJ}$ and $\Delta S^0 = -44.1 \text{ J/K}$ Calculate ΔG^0 for the reaction, and predict whether the reaction will occur spontaneously.
29. The equilibrium constant for a reaction is 10. Calculate ΔG^0 , $T = 300 \text{ K}$, $R = 8.314 \text{ J/K mol}$
30. Calculate the value of ΔG^0 for the conversion of Oxygen to Ozone, $\frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{O}_3(\text{g})$ at 298 K , if K_p for this conversion is 2.47×10^{-29} .
31. Find out the value of equilibrium constant for the following reaction at 298 K.
 $2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g}) \rightarrow \text{NH}_2\text{CONH}_2(\text{aq}) + \text{H}_2\text{O}(l)$

Standard Gibbs energy change, $\Delta_r G^0$ at the given temperature is $-13.6 \text{ kJ mol}^{-1}$.

32. Calculate the entropy change in surroundings when 1.00 mol of $\text{H}_2\text{O(l)}$ is formed under standard conditions. $\Delta_f H^0 = -286 \text{ kJ mol}^{-1}$.

33 What is meant by entropy? Predict the sign of entropy change (ΔS) in each of the following:

- (a) Temperature of crystalline solid is raised from 0K to 115 K
- (b) A liquid crystallizes into solid
- (c) $2 \text{ NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O(g)} + \text{CO}_2(\text{g})$
- (d) $2 \text{ SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
- (e) $\text{H}_2(\text{at } 298\text{K}, 1 \text{ atm}) \rightarrow \text{H}_2(\text{at } 298\text{K}, 10 \text{ atm})$
- (f) $\text{H}_2\text{O(at } 298\text{K, 1 atm}) \rightarrow \text{H}_2\text{O (at } 330\text{K, 1 atm})$
- (g) $2 \text{ NH}_4\text{NO}_3(\text{s}) \xrightarrow{\text{at 1 atm & 373K}} 2 \text{ N}_2(\text{g}) + 4 \text{ H}_2\text{O} + \text{O}_2(\text{g})$
- (h) When rubber band is stretched.
- (i) When an egg is boiled
- (j) $\text{C(graphite)} \rightarrow \text{C(diamond)}$
- (k) $\text{I}_2(\text{g}) \rightarrow \text{I}_2(\text{s})$
- (l) $\text{Hg(l)} \rightarrow \text{Hg(g)}$
- (m) $\text{AgNO}_3(\text{s}) \rightarrow \text{AgNO}_3(\text{aq})$
- (n) Dissolution of iodine in a solvent
- (o) A partition is removed to allow two gases to mix
- (p) HCl is added to AgNO_3 solution and precipitate of AgCl is obtained
- (q) crystallization of copper sulphate from its saturated solution

34 Give reasons for the following:

- (a) A real crystal has more entropy than an ideal crystal
- (b) The dissolution of NH_4Cl in water is endothermic still it dissolves in water .
- (c) Why does a mole of water at 0°C have greater entropy than a mole of ice at 0°C ?
- (d) Neither “q” nor “w” is a state function but “q+w” is a state function.
- (e) Thermodynamically an exothermic reaction is sometimes not spontaneous.
- (f) The entropy of steam is more than that of water at its boiling point.

- (g) The equilibrium constant for a reaction is greater than one if $\Delta_f G^0$ for it is less than zero .
- (h) Endothermic reactions are carried out at higher temperature.
- (i) Evaporation of water is endothermic process but spontaneous .
- (j) When an ideal gas expands in vacuum, there is neither absorption nor evolution of heat .
- (k) Why does entropy of a solid increase on fusion ?
- (l) Why a non-spontaneous reaction becomes spontaneous when coupled with a suitable spontaneous reaction ?
- (m) why for predicting the spontaneity of a reaction , free energy criteria is better than the entropy criteria ?
- (n) Why internal energy is a state function but work is not ?
- (o) Why is standard heat of formation of diamond not zero although it is an element ?
- (p) Why is entropy of a solution higher than that of pure liquid ?
- (q) acetic acid and hydrochloric acid react with KOH solution . The enthalpy of neutralization of acetic acid is -55.8 kJ per mole while that of hydrochloric acid is -57.3 kJ/mol. Why?

35 Justify the following statements

- (a) An exothermic reaction is always thermodynamically spontaneous .why?
- (b)The entropy of a substance increases on going from liquid to vapour state at any temperature.
- (c) At low temperatures enthalpy change dominates ΔG expression and at high temperatures it is the entropy which dominate the value of ΔG .
- (d) Many thermodynamically feasible reactions do not occur under ordinary conditions.
- (e) Reactions with $\Delta G^0 < 0$ always have an equilibrium constant greater than one.

36 Define.../ Discuss the following terms:(Give examples and chemical equation wherever necessary)

Standard enthalpy of combustion

(b) Lattice enthalpy (c) Enthalpy of solution

(d) Standard enthalpy fusion / vapourisation / sublimation (e) Enthalpy of atomization

(f) Bond enthalpy for diatomic and polyatomic molecule. (g) Calorific value (h) Enthalpy of Neutralisation .

(i) State variables/ state functions (j) System (k) work (l) isobaric and isochoric process.

37Differentiate between the following (with examples)

(a) Intensive and extensive properties

(b) Enthalpy of formation and Enthalpy of reaction.

(c) Enthalpy and Internal energy (d) Heat capacity and specific heat capacity.

(e) Reversible and Irreversible process (f) Adiabatic and Isothermal process.

(g) State function and path function (h) Exothermic and Endothermic reaction.

(i) Isolated, Open, Closed, Adiabatic Systems (j) Heat and Work.

7. Equilibrium(Part-I)

Some Important Points and Terms of the Chapter

1. **Equilibrium** represents the state of a process in which the properties like temperature, pressure etc do not show any change with the passage of time
2. **Chemical equilibrium:** When the rates of the forward and reverse reactions become equal, the concentrations of the reactants and the products remain constant. This is the stage of chemical equilibrium. This equilibrium is *dynamic* in nature as it consists of a *forward* reaction in which the reactants give product(s) and *reverse* reaction in which product(s) gives the original reactants. Equilibrium is possible only in a closed system at a given temperature. A mixture of reactants and products in the equilibrium state is called an equilibrium mixture.
3. In a **Homogeneous system**, all the reactants and products are in the same phase. For example, in the gaseous reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, reactants and products are in the homogeneous phase.
4. Equilibrium in a system having more than one phase is called **heterogeneous equilibrium**. The equilibrium between water vapor and liquid water in a closed container is an example of heterogeneous equilibrium. $H_2O(l) \rightleftharpoons H_2O(g)$

5. **Henry Law**:-It states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent
6. **Law of Chemical Equilibrium:** It may be stated as, at a given temperature the ratio of product of equilibrium concentration of the products to that of the reactants with each concentration terms raised to power equal to the respective stoichiometric coefficient in the balanced chemical reaction has a constant value. This constant value is known as Equilibrium constant. For a general reaction of the type $aA + bB \rightleftharpoons cC + dD$

$K_c = [C]^c[D]^d/[A]^a[B]^b$ This expression is known as Law Of Chemical Equilibrium

7. **Relationship between K_p and K_c :** $K_p = K_c(RT)^{\Delta n}$
8. **Units of Equilibrium Constant:** The value of equilibrium constant K_c can be calculated by substituting the concentration terms in mol/L and for K_p partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same. For the reactions (i) $H_2(g) + I_2(g) \rightarrow 2HI$, K_c and K_p have no unit.(ii) $N_2O_4(g) \rightarrow 2NO_2(g)$, K_c has unit mol/L and K_p has unit bar

9. Characteristics Of Equilibrium Constant

- Equilibrium constant is applicable only when concentrations of the reactants and products have attained their equilibrium state.
- The value of equilibrium constant is independent of initial concentrations of the reactants and products.
- Equilibrium constant is temperature dependent having one unique value for a particular reaction represented by a balanced equation at a given temperature.
- The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction.
- The equilibrium constant K for a reaction is related to the equilibrium constant of the corresponding reaction, whose equation is obtained by multiplying or dividing the equation for the original reaction by a small integer.

10. Applications of equilibrium constant :

- Predict the extent of a reaction on the basis of its magnitude.

- Predict the direction of the reaction, and
- Calculate equilibrium concentrations.

11. Le Chatelier's Principle: It states that if a system in equilibrium is subjected to a change of concentration, temperature or pressure, the equilibrium shifts in a direction that tends to undo the effect of the change imposed.

- **Effect of change of concentration:** When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimize the effect of concentration change. For eg:- $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

If H_2 is added to the reaction mixture at equilibrium, the equilibrium of the reaction is disturbed. In order to restore it, the reaction proceeds in a direction whereas H_2 is consumed i.e more of H_2 and I_2 react to form HI and finally the equilibrium shifts in forward direction.

- **Effect of change of pressure:** When the pressure is increased the equilibrium shifts in the direction in which the number of moles of the gas decreases.

Consider the reaction, $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$ Here, 4 mol of gaseous reactants ($CO + 3H_2$) become 2 mol of gaseous products ($CH_4(g) + H_2O$). so by Le Chatelier's principle. The increase in pressure will shift the equilibrium in the forward direction, a direction in which the number of moles of the gas or pressure decreases.

- **Effect of change of Temperature:** When a change in temperature occurs, the value of equilibrium constant changes. In general, the temperature dependence of the equilibrium constant depends on the sign of ΔH for the reaction. The equilibrium constant for an exothermic reaction (-ve ΔH) decreases as the temperature increases. The equilibrium constant for an endothermic reaction (+ve ΔH) increases as the temperature increases. When the Temperature is increased the equilibrium shifts in the direction in of endothermic reaction.

Consider a reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92.38\text{Kj/mol}$

According to Le Chatelier's principle, raising the temperature shifts the equilibrium to left (backward direction i.e direction of endothermic reaction) and decreases the equilibrium concentration of ammonia.

- **Effect of Inert Gas Addition:** If the volume is kept constant and an inert gas such as argon is added which does not take part in the reaction, the equilibrium remains undisturbed. It is because the addition of an inert gas at constant volume does not change the partial pressures or the molar concentrations of the substance involved in the reaction. The reaction quotient changes only if the added gas is a reactant or product involved in the reaction.
- **Effect of a Catalyst:** A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products. It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium. Catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression.

Summary of Le Chatelier's Principle

| Type of Effect or Change | Direction of Equilibrium |
|----------------------------|---|
| Addition of more reactants | Forward direction |
| Addition of more products | Backward direction |
| Increase in temperature | Towards endothermic reaction |
| Decrease in temperature | Towards exothermic reaction |
| Addition of Catalyst | No effect |
| Increase in Pressure | where the no. of gaseous moles are less |
| Decrease in Pressure | where the no. of gaseous moles are more |

| | |
|---|---|
| Addition of Inert gas at const.Volume | No effect |
| Addition of Inert gas at const.pressure | where the no. of gaseous moles are more |

Unit-7

EQUILIBRIUM(Part-I)

1. Question based on law of chemical equilibrium, Equilibrium constant, Applications of Equilibrium Constants, Relation Between K_p & K_c .

1. What do mean by law of chemical equilibrium? Explain with an example.

2. Write the expression for the equilibrium constant, K_c for each of the following reactions:
- $2\text{NOCl}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g})$
 - $2\text{Cu}(\text{NO}_3)_2(\text{s}) \rightleftharpoons 2\text{CuO}(\text{s}) + 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
 - $\text{CH}_3\text{COOC}_2\text{H}_5(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOH}(\text{aq}) + \text{C}_2\text{H}_5\text{OH}(\text{aq})$
 - $\text{Fe}^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq}) \rightleftharpoons \text{Fe}(\text{OH})_3(\text{s})$
 - $\text{I}_2(\text{s}) + 5\text{F}_2 \rightleftharpoons 2\text{IF}_5$
3. Find out the value of K_c for each of the following equilibria from the value of K_p :
- $2\text{NOCl}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}); K_p = 1.8 \times 10^{-2}$ at 500 K
 - $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g}); K_p = 167$ at 1073 K
4. Write the balanced chemical equation corresponding to this equilibrium constant expression for a gas reaction.
- $$K_c = \frac{[\text{NH}_3]^4 [\text{O}_2]^5}{[\text{NO}]^4 [\text{H}_2\text{O}]^6}$$
5. What is K_c for the following equilibrium when the equilibrium concentration of each substance is: $[\text{SO}_2] = 0.60\text{M}$, $[\text{O}_2] = 0.82\text{M}$ and $[\text{SO}_3] = 1.90\text{M}$
- $$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$$
6. The following concentrations were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500K. $[\text{N}_2] = 1.5 \times 10^{-2}\text{M}$. $[\text{H}_2] = 3.0 \times 10^{-2}\text{M}$ and $[\text{NH}_3] = 1.2 \times 10^{-2}\text{M}$. Calculate equilibrium constant.
7. At equilibrium, the concentrations of $\text{N}_2 = 3.0 \times 10^{-3}\text{M}$, $\text{O}_2 = 4.2 \times 10^{-3}\text{M}$ and $\text{NO} = 2.8 \times 10^{-3}\text{M}$ in a sealed vessel at 800K. What will be K_c for the reaction: $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
8. PCl_5 , PCl_3 and Cl_2 are at equilibrium at 500 K and having concentration 1.59M PCl_3 , 1.59M Cl_2 and 1.41 M PCl_5 . Calculate K_c for the reaction, $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$
9. For the equilibrium, $2\text{NOCl}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g})$ the value of the equilibrium constant, K_c is 3.75×10^{-6} at 1069 K. Calculate the K_p for the reaction at this temperature?

2. Question based on Calculating Equilibrium Concentrations, Le Chatelier's principle

Effect of Pressure Change, Concentration Change, Temperature Change, Inert Gas Addition & Catalyst

10. The value of $K_c = 4.24$ at 800K for the reaction,



$+ \text{H}_2\text{O (g)} \rightleftharpoons \text{CO}_2 (g) + \text{H}_2 (g)$ Calculate equilibrium concentrations of CO_2 , H_2 , CO and H_2O at 800 K, if only CO and H_2O are present initially at concentrations of 0.10M each. The value of K_p for the reaction, $\text{CO}_2 (g) + \text{C (s)} \rightleftharpoons 2\text{CO (g)}$ is 3.0 at 1000 K. If initially $p \text{ CO}_2 = 0.48$ bar and $p \text{ CO} = 0$ bar and puregraphite is present, calculate the equilibrium partial pressures of CO and CO_2 .

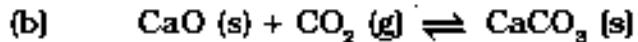
11. A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K.

After equilibrium was attained, concentration of PCl_5 was found to be $0.5 \times 10^{-1} \text{ mol L}^{-1}$. If value of K_c is 8.3×10^{-3} , what are the concentrations of PCl_3 and Cl_2 at equilibrium?



12. What do you mean by Lechatelier's principle? Explain with an example?

13. Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?

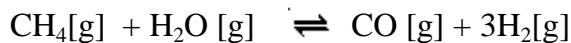


14. Which of the following reactions will get affected by increasing the pressure? Also, mention whether change will cause the reaction to go into

forward or backward direction.

- (I) $\text{COCl}_2 (\text{g}) \rightleftharpoons \text{CO} (\text{g}) + \text{Cl}_2 (\text{g})$
- (II) $\text{CH}_4 (\text{g}) + 2\text{S}_2 (\text{g}) \rightleftharpoons \text{CS}_2 (\text{g}) + 2\text{H}_2\text{S} (\text{g})$
- (III) $\text{CO}_2 (\text{g}) + \text{C} (\text{s}) \rightleftharpoons 2\text{CO} (\text{g})$
- (IV) $2\text{H}_2 (\text{g}) + \text{CO} (\text{g}) \rightleftharpoons \text{CH}_3\text{OH} (\text{g})$
- (V) $\text{CaCO}_3 (\text{s}) \rightleftharpoons \text{CaO} (\text{s}) + \text{CO}_2 (\text{g})$
- (VI) $4 \text{NH}_3 (\text{g}) + 5\text{O}_2 (\text{g}) \rightleftharpoons 4\text{NO} (\text{g}) + 6\text{H}_2\text{O} (\text{g})$

15. Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:



- a) Write an expression for K_p for the above reaction.
- b) How will the values of K_p and the composition of equilibrium mixture be affected by
 - i) Increasing the pressure
 - ii) Increasing the temperature
 - iii) Using a catalyst

16. Describe the effect of: - a) Addition of H_2 b) Addition of CH_3OH c) Removal of CO d) Removal of CH_3OH On the equilibrium of the reaction: $2 \text{H}_2 [\text{g}] + \text{CO} [\text{g}] \rightleftharpoons \text{CH}_3\text{OH} [\text{g}]$

17. At 473 K, equilibrium constant K_c for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3} . If decomposition is depicted as, $\text{PCl}_5 (\text{g}) \rightleftharpoons \text{PCl}_3 (\text{g}) + \text{Cl}_2 (\text{g}) \Delta_r H^0 = 124.0 \text{ kJ mol}^{-1}$

- a) write an expression for K_c for the reaction.
- b) what is the value of K_c for the reverse reaction at the same temperature. c) what would be the effect on K_c if (i) more PCl_5 is added (ii) pressure is increased (iii) the temperature is increased ?

3. Question based on Relationship Between Equilibrium Constant K, And Gibbs Energy G

18. The value of ΔG^0 for the phosphorylation of glucose in glycolysis is 13.8 kJ / mol. Find the value of K_c at 298 K
19. Hydrolysis of sucrose gives, Sucrose + H₂O ⇌ Glucose + Fructose
Equilibrium constant K_c for the reaction is 2×10^{13} at 300K. Calculate ΔG^0 at 300K.
20. Calculate a) ΔG^0 and b) the equilibrium constant for the formation of NO₂ from NO and O₂ at 298K NO (g) + $\frac{1}{2}$ O₂ (g) ⇌ NO₂ (g) where $\Delta_f G^0$ (NO₂) = 52.0 kJ/mol $\Delta_f G^0$ (NO) = 87.0 kJ/mol $\Delta_f G^0$ (O₂) = 0 kJ/mol.

Question 7.1:

A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.

- a) *What is the initial effect of the change on vapour pressure?*
- b) *How do rates of evaporation and condensation change initially?*
- c) *What happens when equilibrium is restored finally and what will be the final vapour pressure?*

• **Answer**

(a) If the volume of the container is suddenly increased, then the vapour pressure would decrease initially. This is because the amount of vapour remains the same, but the volume increases suddenly. As a result, the same amount of vapour is distributed in a larger volume.

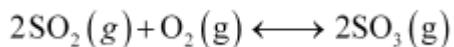
(b) Since the temperature is constant, the rate of evaporation also remains constant. When the volume of the container is increased, the density of the vapour phase decreases. As a result, the rate of collisions of the vapour particles also decreases. Hence, the rate of condensation decreases initially.

(c) When equilibrium is restored finally, the rate of evaporation becomes equal to the rate of condensation. In this case, only the volume changes while the

temperature remains constant. The vapour pressure depends on temperature and not on volume. Hence, the final vapour pressure will be equal to the original vapour pressure of the system.

Question 7.2:

What is K_c for the following equilibrium when the equilibrium concentration of each substance is: $[SO_2] = 0.60\text{ M}$, $[O_2] = 0.82\text{ M}$ and $[SO_3] = 1.90\text{ M}$?



• **Answer**

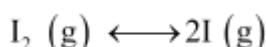
The equilibrium constant (K_c) for the given reaction is:

$$\begin{aligned} K_c &= \frac{[SO_3]^2}{[SO_2]^2 [O_2]} \\ &= \frac{(1.90)^2 \text{ M}^2}{(0.60)^2 (0.821) \text{ M}^3} \\ &= 12.239 \text{ M}^{-1} (\text{approximately}) \end{aligned}$$

Hence, K_c for the equilibrium is 12.239 M^{-1} .

Question 7.3:

At a certain temperature and total pressure of 10^5 Pa , iodine vapour contains 40% by volume of I atoms



Calculate K_p for the equilibrium.

• **Answer**

Partial pressure of I atoms,

$$\begin{aligned} p_I &= \frac{40}{100} \times p_{\text{total}} \\ &= \frac{40}{100} \times 10^5 \\ &= 4 \times 10^4 \text{ Pa} \end{aligned}$$

Partial pressure of I_2 molecules,

$$p_{I_2} = \frac{60}{100} \times p_{\text{total}}$$

$$= \frac{60}{100} \times 10^5$$

$$= 6 \times 10^4 \text{ Pa}$$

Now, for the given reaction,

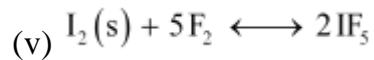
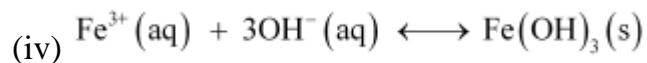
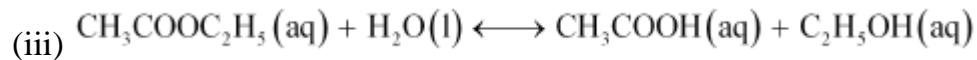
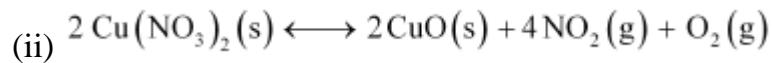
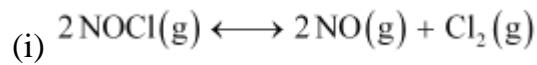
$$K_p = \frac{(pI)^2}{p_{I_2}}$$

$$= \frac{(4 \times 10^4)^2 \text{ Pa}^2}{6 \times 10^4 \text{ Pa}}$$

$$= 2.67 \times 10^4 \text{ Pa}$$

Question 7.4:

Write the expression for the equilibrium constant, K_c for each of the following reactions:



• **Answer**

$$(i) \quad K_c = \frac{[\text{NO}_{(g)}]^2 [\text{Cl}_{2(g)}]}{[\text{NOCl}_{(g)}]^2}$$

$$(ii) \quad K_c = \frac{[\text{CuO}_{(s)}]^2 [\text{NO}_{2(g)}]^4 [\text{O}_{2(g)}]}{[\text{Cu}(\text{NO}_3)_{2(s)}]^2}$$

$$= [\text{NO}_{2(g)}]^4 [\text{O}_{2(g)}]$$

$$(iii) \quad K_c = \frac{[\text{CH}_3\text{COOH}_{(aq)}][\text{C}_2\text{H}_5\text{OH}_{(aq)}]}{[\text{CH}_3\text{COOC}_2\text{H}_{5(aq)}][\text{H}_2\text{O}_{(l)}]} = \frac{[\text{CH}_3\text{COOH}_{(aq)}][\text{C}_2\text{H}_5\text{OH}_{(aq)}]}{[\text{CH}_3\text{COOC}_2\text{H}_{5(aq)}]}$$

$$(iv) \quad K_c = \frac{[\text{Fe(OH)}_{3(s)}]}{[\text{Fe}^{3+}_{(aq)}][\text{OH}^-_{(aq)}]^3}$$

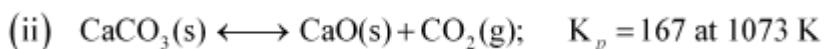
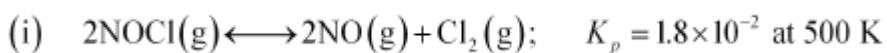
$$= \frac{1}{[\text{Fe}^{3+}_{(aq)}][\text{OH}^-_{(aq)}]^3}$$

$$(v) \quad K_c = \frac{[\text{IF}_5]^2}{[\text{I}_{2(s)}][\text{F}_2]^5}$$

$$= \frac{[\text{IF}_5]^2}{[\text{F}_2]^5}$$

Question 7.5:

Find out the value of K_c for each of the following equilibria from the value of K_p :



• Answer

The relation between K_p and K_c is given as:

$$K_p = K_c (RT)^{\Delta n}$$

(a) Here,

$$\Delta n = 3 - 2 = 1$$

$$R = 0.0831 \text{ barLmol}^{-1}\text{K}^{-1}$$

$$T = 500 \text{ K}$$

$$K_p = 1.8 \times 10^{-2}$$

Now,

$$\begin{aligned} K_p &= K_c (RT)^{\Delta n} \\ \Rightarrow 1.8 \times 10^{-2} &= K_c (0.0831 \times 500)^1 \\ \Rightarrow K_c &= \frac{1.8 \times 10^{-2}}{0.0831 \times 500} \\ &= 4.33 \times 10^{-4} \text{ (approximately)} \end{aligned}$$

(b) Here,

$$\Delta n = 2 - 1 = 1$$

$$R = 0.0831 \text{ barLmol}^{-1}\text{K}^{-1}$$

$$T = 1073 \text{ K}$$

$$K_p = 167$$

Now,

$$\begin{aligned} K_p &= K_c (RT)^{\Delta n} \\ \Rightarrow 167 &= K_c (0.0831 \times 1073)^{\Delta n} \\ \Rightarrow K_c &= \frac{167}{0.0831 \times 1073} \\ &= 1.87 \text{ (approximately)} \end{aligned}$$

Question 7.6:

For the following equilibrium, $K_c = 6.3 \times 10^{14}$ at 1000 K



Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_c , for the reverse reaction?

• **Answer**

It is given that K_c for the forward reaction is 6.3×10^{14} .

Then, K_c for the reverse reaction will be,

$$K'_c = \frac{1}{K_c}$$

$$= \frac{1}{6.3 \times 10^{14}}$$

$$= 1.59 \times 10^{-15}$$

Question 7.7:

Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression?

- **Answer**

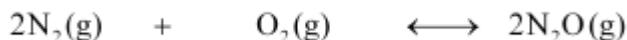
For a pure substance (both solids and liquids),

$$\begin{aligned} [\text{Pure substance}] &= \frac{\text{Number of moles}}{\text{Volume}} \\ &= \frac{\text{Mass}/\text{molecular mass}}{\text{Volume}} \\ &= \frac{\text{Mass}}{\text{Volume} \times \text{Molecular mass}} \\ &= \frac{\text{Density}}{\text{Molecular mass}} \end{aligned}$$

Now, the molecular mass and density (at a particular temperature) of a pure substance is always fixed and is accounted for in the equilibrium constant. Therefore, the values of pure substances are not mentioned in the equilibrium constant expression.

Question 7.8:

Reaction between N₂ and O₂ takes place as follows:

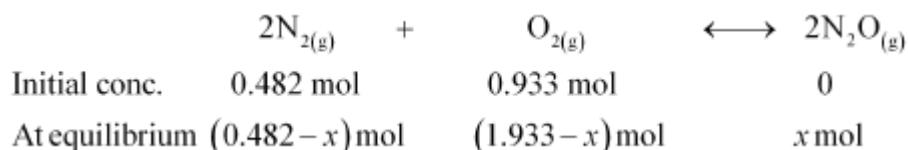


If a mixture of 0.482 mol of N₂ and 0.933 mol of O₂ is placed in a 10 L reaction vessel and allowed to form N₂O at a temperature for which K_c = 2.0 × 10⁻³⁷, determine the composition of equilibrium mixture.

- **Answer**

Let the concentration of N₂O at equilibrium be x .

The given reaction is:



Therefore, at equilibrium, in the 10 L vessel:

$$[\text{N}_2] = \frac{0.482-x}{10}, [\text{O}_2] = \frac{0.933-x/2}{10}, [\text{N}_2\text{O}] = \frac{x}{10}$$

The value of equilibrium constant i.e., $K_c = 2.0 \times 10^{-37}$ is very small. Therefore, the amount of N₂ and O₂ reacted is also very small. Thus, x can be neglected from the expressions of molar concentrations of N₂ and O₂.

Then,

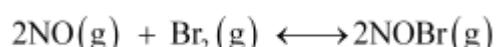
$$[\text{N}_2] = \frac{0.482}{10} = 0.0482 \text{ mol L}^{-1} \text{ and } [\text{O}_2] = \frac{0.933}{10} = 0.0933 \text{ mol L}^{-1}$$

Now,

$$\begin{aligned}
 K_c &= \frac{[\text{N}_2\text{O}_{(g)}]^2}{[\text{N}_{2(g)}]^2 [\text{O}_{2(g)}]} \\
 \Rightarrow 2.0 \times 10^{-37} &= \frac{\left(\frac{x}{10}\right)^2}{(0.0482)^2 (0.0933)} \\
 \Rightarrow \frac{x^2}{100} &= 2.0 \times 10^{-37} \times (0.0482)^2 \times (0.0933) \\
 \Rightarrow x^2 &= 43.35 \times 10^{-40} \\
 \Rightarrow x &= 6.6 \times 10^{-20} \\
 [\text{N}_2\text{O}] &= \frac{x}{10} = \frac{6.6 \times 10^{-20}}{10} \\
 &= 6.6 \times 10^{-21}
 \end{aligned}$$

Question 7.9:

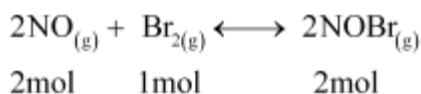
Nitric oxide reacts with Br₂ and gives nitrosyl bromide as per reaction given below:



When 0.087 mol of NO and 0.0437 mol of Br_2 are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of NO and Br_2 .

• **Answer**

The given reaction is:



Now, 2 mol of NOBr are formed from 2 mol of NO. Therefore, 0.0518 mol of NOBr are formed from 0.0518 mol of NO.

Again, 2 mol of NOBr are formed from 1 mol of Br_2 .

$$\frac{0.0518}{2}$$

Therefore, 0.0518 mol of NOBr are formed from $\frac{0.0518}{2}$ mol of Br_2 , or 0.0259 mol of NO

The amount of NO and Br_2 present initially is as follows:

$$[\text{NO}] = 0.087 \text{ mol} \quad [\text{Br}_2] = 0.0437 \text{ mol}$$

Therefore, the amount of NO present at equilibrium is:

$$[\text{NO}] = 0.087 - 0.0518$$

$$= 0.0352 \text{ mol}$$

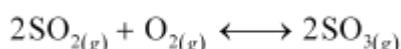
And, the amount of Br_2 present at equilibrium is:

$$[\text{Br}_2] = 0.0437 - 0.0259$$

$$= 0.0178 \text{ mol}$$

Question 7.10:

At 450 K, $K_p = 2.0 \times 10^{10}$ /bar for the given reaction at equilibrium.



What is K_c at this temperature?

• **Answer**

For the given reaction,

$$\Delta n = 2 - 3 = -1$$

$$T = 450 \text{ K}$$

$$R = 0.0831 \text{ bar L bar K}^{-1} \text{ mol}^{-1}$$

$$K_p = 2.0 \times 10^{10} \text{ bar}^{-1}$$

We know that,

$$K_p = K_c (RT) \Delta n$$

$$\Rightarrow 2.0 \times 10^{10} \text{ bar}^{-1} = K_c \left(0.0831 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 450 \text{ K} \right)^{-1}$$

$$\Rightarrow K_c = \frac{2.0 \times 10^{10} \text{ bar}^{-1}}{\left(0.0831 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 450 \text{ K} \right)^{-1}}$$

$$= (2.0 \times 10^{10} \text{ bar}^{-1}) (0.0831 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 450 \text{ K})$$

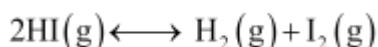
$$= 74.79 \times 10^{10} \text{ L mol}^{-1}$$

$$= 7.48 \times 10^{11} \text{ L mol}^{-1}$$

$$= 7.48 \times 10^{11} \text{ M}^{-1}$$

Question 7.11:

A sample of $\text{HI}_{(g)}$ is placed in flask at a pressure of 0.2 atm. At equilibrium the partial pressure of $\text{HI}_{(g)}$ is 0.04 atm. What is K_p for the given equilibrium?



Answer

The initial concentration of HI is 0.2 atm. At equilibrium, it has a partial pressure of 0.04 atm. Therefore, a decrease in the pressure of HI is $0.2 - 0.04 = 0.16$. The given reaction is:

| | | | | | |
|----------------|--------------------|----------------------|-------------------|------------------|-------------------|
| | $2\text{HI}_{(g)}$ | \rightleftharpoons | $\text{H}_{2(g)}$ | + | $\text{I}_{2(g)}$ |
| Initial conc. | 0.2 atm | | 0 | | 0 |
| At equilibrium | 0.04 atm | | $\frac{0.16}{2}$ | $\frac{2.15}{2}$ | |

$= 0.08 \text{ atm}$ $= 0.08 \text{ atm}$

Therefore,

$$\begin{aligned} K_p &= \frac{P_{\text{H}_2} \times P_{\text{I}_2}}{P_{\text{HI}}^2} \\ &= \frac{0.08 \times 0.08}{(0.04)^2} \\ &= \frac{0.0064}{0.0016} \\ &= 4.0 \end{aligned}$$

Hence, the value of K_p for the given equilibrium is 4.0.

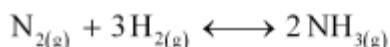
Question 7.12:

A mixture of 1.57 mol of N_2 , 1.92 mol of H_2 and 8.13 mol of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 1.7×10^2

Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

• **Answer**

The given reaction is:



The given concentration of various species is

$$[N_2] = \frac{1.57}{20} \text{ mol L}^{-1} \quad [H_2] = \frac{1.92}{20} \text{ mol L}^{-1}$$

$$[NH_3] = \frac{8.13}{20} \text{ mol L}^{-1}$$

Now, reaction quotient Q_c is:

$$\begin{aligned} Q_c &= \frac{[NH_3]^2}{[N_2][H_2]^3} \\ &= \frac{\left(\frac{8.13}{20}\right)^2}{\left(\frac{1.57}{20}\right)\left(\frac{1.92}{20}\right)^3} \\ &= 2.4 \times 10^3 \end{aligned}$$

Since $Q_c \neq K_c$, the reaction mixture is not at equilibrium.

Again, $Q_c > K_c$. Hence, the reaction will proceed in the reverse direction.

Question 7.13:

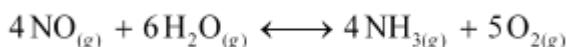
The equilibrium constant expression for a gas reaction is,

$$K_c = \frac{[NH_3]^4 [O_2]^5}{[NO]^4 [H_2O]^6}$$

Write the balanced chemical equation corresponding to this expression.

• **Answer**

The balanced chemical equation corresponding to the given expression can be written as:



Question 7.14:

One mole of H₂O and one mole of CO are taken in 10 L vessel and heated to 725 K. At equilibrium 40% of water (by mass) reacts with CO according to the equation,



Calculate the equilibrium constant for the reaction.

• **Answer**

The given reaction is:

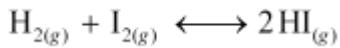
| | H ₂ O _(g) | + | CO _(g) | ↔ | H _{2(g)} | + | CO _{2(g)} |
|----------------|--|---|--|---|--|---|--|
| Initial conc. | $\frac{1}{10}\text{M}$ | | $\frac{1}{10}\text{M}$ | | 0 | | 0 |
| At equilibrium | $\frac{1-0.4}{10}\text{M}$ $= 0.06\text{M}$ | | $\frac{1-0.4}{10}\text{M}$ $= 0.06\text{M}$ | | $\frac{0.4}{10}\text{M}$ $= 0.04\text{M}$ | | $\frac{0.4}{10}\text{M}$ $= 0.04\text{M}$ |

Therefore, the equilibrium constant for the reaction,

$$\begin{aligned}K_c &= \frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]} \\&= \frac{0.04 \times 0.04}{0.06 \times 0.06} \\&= 0.444 \text{ (approximately)}\end{aligned}$$

Question 7.15:

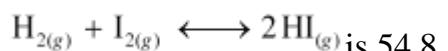
At 700 K, equilibrium constant for the reaction



is 54.8. If 0.5 molL⁻¹ of HI_(g) is present at equilibrium at 700 K, what are the concentration of H_{2(g)} and I_{2(g)} assuming that we initially started with HI_(g) and allowed it to reach equilibrium at 700 K?

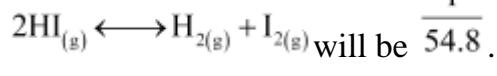
• **Answer**

It is given that equilibrium constant K_c for the reaction



is 54.8.

Therefore, at equilibrium, the equilibrium constant K'_c for the reaction



$$[HI] = 0.5 \text{ mol L}^{-1}$$

Let the concentrations of hydrogen and iodine at equilibrium be $x \text{ mol L}^{-1}$

$$[H_2] = [I_2] = x \text{ mol L}^{-1}$$

$$\text{Therefore, } \frac{[H_2][I_2]}{[HI]^2} = K'_c$$

$$\Rightarrow \frac{x \times x}{(0.5)^2} = \frac{1}{54.8}$$

$$\Rightarrow x^2 = \frac{0.25}{54.8}$$

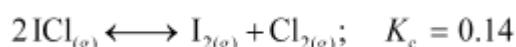
$$\Rightarrow x = 0.06754$$

$$x = 0.068 \text{ mol L}^{-1} \text{ (approximately)}$$

Hence, at equilibrium, $[H_2] = [I_2] = 0.068 \text{ mol L}^{-1}$.

Question 7.16:

What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M?



• **Answer**

The given reaction is:

| | | | |
|----------------|----------------------|------------|-------------|
| $2ICl_{(g)}$ | \rightleftharpoons | $I_{2(g)}$ | $Cl_{2(g)}$ |
| Initial conc. | 0.78 M | 0 | 0 |
| At equilibrium | $(0.78 - 2x)$ M | x M | x M |

Now, we can write, $\frac{[I_2][Cl_2]}{[ICl]^2} = K_c$

$$\Rightarrow \frac{x \times x}{(0.78 - 2x)^2} = 0.14$$

$$\Rightarrow \frac{x^2}{(0.78 - 2x)^2} = 0.14$$

$$\Rightarrow \frac{x}{0.78 - 2x} = 0.374$$

$$\Rightarrow x = 0.292 - 0.748x$$

$$\Rightarrow 1.748x = 0.292$$

$$\Rightarrow x = 0.167$$

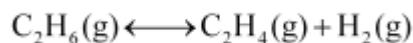
Hence, at equilibrium,

$$[H_2] = [I_2] = 0.167 \text{ M}$$

$$\begin{aligned}[HI] &= (0.78 - 2 \times 0.167) \text{ M} \\ &= 0.446 \text{ M}\end{aligned}$$

Question 7.17:

$K_p = 0.04 \text{ atm at } 899 \text{ K}$ for the equilibrium shown below. What is the equilibrium concentration of C_2H_6 when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium?



• **Answer**

Let p be the pressure exerted by ethene and hydrogen gas (each) at equilibrium.

Now, according to the reaction,

| | $C_2H_{6(g)}$ | \rightleftharpoons | $C_2H_{4(g)}$ | $+$ | $H_{2(g)}$ |
|----------------|---------------|----------------------|---------------|-----|------------|
| Initial conc. | 4.0 atm | | 0 | | 0 |
| At equilibrium | $4.0 - p$ | | p | | p |

We can write,

$$\frac{p_{C_2H_4} \times p_{H_2}}{p_{C_2H_6}} = K_p$$

$$\Rightarrow \frac{p \times p}{40 - p} = 0.04$$

$$\Rightarrow p^2 = 0.16 - 0.04p$$

$$\Rightarrow p^2 + 0.04p - 0.16 = 0$$

$$\text{Now, } p = \frac{-0.04 \pm \sqrt{(0.04)^2 - 4 \times 1 \times (-0.16)}}{2 \times 1}$$

$$= \frac{-0.04 \pm 0.80}{2}$$

$$= \frac{0.76}{2} \quad (\text{Taking positive value})$$

$$= 0.38$$

Hence, at equilibrium,

$$[C_2H_6] - 4 - p = 4 - 0.38 \\ = 3.62 \text{ atm}$$

Question 7.18:

Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as:



- (i) *Write the concentration ratio (reaction quotient), Q_c , for this reaction (note: water is not in excess and is not a solvent in this reaction)*
- (ii) *At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.*
- (iii) *Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after sometime. Has equilibrium been reached?*

• **Answer**

$$(i) \text{ Reaction quotient, } Q_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

- (ii) Let the volume of the reaction mixture be V . Also, here we will consider that water is a solvent and is present in excess.

The given reaction is:

| | | | | | |
|----------------|--|---|-----------------------|--|-----------------------------|
| | $\text{CH}_3\text{COOH}_{(l)}$ | $+\text{C}_2\text{H}_5\text{OH}_{(l)}$ | \longleftrightarrow | $\text{CH}_3\text{COOC}_2\text{H}_5{}_{(l)}$ | $+\text{H}_2\text{O}_{(l)}$ |
| Initial conc. | $\frac{1}{V}\text{M}$ | $\frac{0.18}{V}\text{M}$ | | 0 | 0 |
| At equilibrium | $\frac{1-0.171}{V}$ $= \frac{0.829}{V}\text{M}$ | $\frac{0.18-0.171}{V}$ $= \frac{0.009}{V}\text{M}$ | | $\frac{0.171}{V}\text{M}$ | $\frac{0.171}{V}\text{M}$ |

Therefore, equilibrium constant for the given reaction is:

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

$$= \frac{\frac{0.171}{V} \times \frac{0.171}{V}}{\frac{0.829}{V} \times \frac{0.009}{V}} = 3.919$$

$$= 3.92 \text{ (approximately)}$$

(iii) Let the volume of the reaction mixture be V .

| | | | | | |
|-----------------|---|--|-----------------------|--|-----------------------------|
| | $\text{CH}_3\text{COOH}_{(l)}$ | $+\text{C}_2\text{H}_5\text{OH}_{(l)}$ | \longleftrightarrow | $\text{CH}_3\text{COOC}_2\text{H}_5{}_{(l)}$ | $+\text{H}_2\text{O}_{(l)}$ |
| Initial conc. | $\frac{1.0}{V}\text{M}$ | $\frac{0.5}{V}\text{M}$ | | 0 | 0 |
| After some time | $\frac{10-0.214}{V}$ $= \frac{0.786}{V}\text{M}$ | $\frac{0.5-0.214}{V}$ $= \frac{0.286}{V}\text{M}$ | | $\frac{0.214}{V}\text{M}$ | $\frac{0.214}{V}\text{M}$ |

Therefore, the reaction quotient is,

$$Q_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

$$= \frac{\frac{0.214}{V} \times \frac{0.214}{V}}{\frac{0.786}{V} \times \frac{0.286}{V}}$$

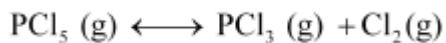
$$= 0.2037$$

$$= 0.204 \text{ (approximately)}$$

Since $Q_c < K_c$, equilibrium has not been reached.

Question 7.19:

A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be $0.5 \times 10^{-1} \text{ mol L}^{-1}$. If value of K_c is 8.3×10^{-3} , what are the concentrations of PCl_3 and Cl_2 at equilibrium?



• **Answer**

Let the concentrations of both PCl_3 and Cl_2 at equilibrium be $x \text{ mol L}^{-1}$. The given reaction is:



At equilibrium $0.5 \times 10^{-1} \text{ mol L}^{-1}$ $x \text{ mol L}^{-1}$ $x \text{ mol L}^{-1}$

It is given that the value of equilibrium constant, K_c is 8.3×10^{-3} .

Now we can write the expression for equilibrium as:

$$\frac{[\text{PCl}_2][\text{Cl}_2]}{[\text{PCl}_5]} = K_c$$

$$\Rightarrow \frac{x \times x}{0.5 \times 10^{-1}} = 8.3 \times 10^{-3}$$

$$\Rightarrow x^2 = 4.15 \times 10^{-4}$$

$$\Rightarrow x = 2.04 \times 10^{-2}$$

$$= 0.0204$$

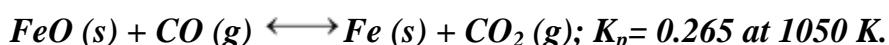
$$= 0.02 \text{ (approximately)}$$

Therefore, at equilibrium,

$$[\text{PCl}_3] = [\text{Cl}_2] = 0.02 \text{ mol L}^{-1}.$$

Question 7.20:

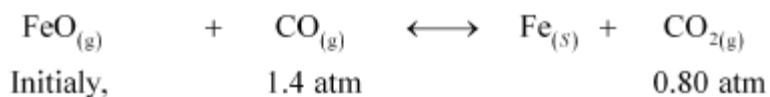
One of the reactions that take place in producing steel from iron ore is the reduction of iron (II) oxide by carbon monoxide to give iron metal and CO_2 .



What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are: $p_{\text{CO}} = 1.4 \text{ atm}$ and $p_{\text{CO}_2} = 0.80 \text{ atm}$?

• **Answer**

For the given reaction,



$$Q_p = \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \\ = \frac{0.80}{1.4} \\ = 0.571$$

It is given that $K_p = 0.265$.

Since $Q_p > K_p$, the reaction will proceed in the backward direction.

Therefore, we can say that the pressure of CO will increase while the pressure of CO_2 will decrease.

Now, let the increase in pressure of CO = decrease in pressure of CO_2 be p .

Then, we can write,

$$K_p = \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \\ \Rightarrow 0.265 = \frac{0.80 - p}{1.4 + p} \\ \Rightarrow 0.371 + 0.265p = 0.80 - p \\ \Rightarrow 1.265p = 0.429 \\ \Rightarrow p = 0.339 \text{ atm}$$

Therefore, equilibrium partial of $\text{CO}_2, p_{\text{CO}_2} = 0.80 - 0.339 = 0.461 \text{ atm}$.

And, equilibrium partial pressure of CO, $p_{\text{CO}} = 1.4 + 0.339 = 1.739 \text{ atm}$.

Question 7.21:

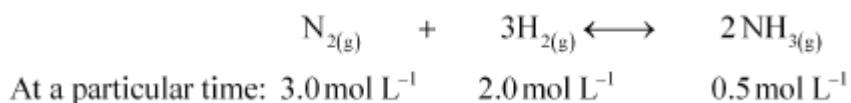
Equilibrium constant, K_c for the reaction



At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L^{-1} N_2 , 2.0 mol L^{-1} H_2 and 0.5 mol L^{-1} NH_3 . Is the reaction at equilibrium? If not in which direction does the reaction tend to proceed to reach equilibrium?

- **Answer**

The given reaction is:



Now, we know that,

$$\begin{aligned} Q_c &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \\ &= \frac{(0.5)^2}{(3.0)(2.0)^3} \\ &= 0.0104 \end{aligned}$$

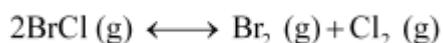
It is given that $K_c = 0.061$.

Since $Q_c \neq K_c$, the reaction is not at equilibrium.

Since $Q_c < K_c$, the reaction will proceed in the forward direction to reach equilibrium.

Question 7.22:

Bromine monochloride, BrCl decomposes into bromine and chlorine and reaches the equilibrium:



for which $K_c = 32$ at 500 K . If initially pure BrCl is present at a concentration of $3.3 \times 10^{-3} \text{ mol L}^{-1}$, what is its molar concentration in the mixture at equilibrium?

• **Answer**

Let the amount of bromine and chlorine formed at equilibrium be x . The given reaction is:

| | | | | |
|-----------------------------|---------------------------|---------------------------|-----|---------------------------|
| $2\text{BrCl}_{(\text{g})}$ | \rightleftharpoons | $\text{Br}_{2(\text{g})}$ | $+$ | $\text{Cl}_{2(\text{g})}$ |
| Initial conc. | 3.3×10^{-3} | 0 | | 0 |
| At equilibrium | $3.3 \times 10^{-3} - 2x$ | x | | x |

Now, we can write,

$$\frac{[\text{Br}_2][\text{Cl}_2]}{[\text{BrCl}]^2} = K_c$$

$$\Rightarrow \frac{x \times x}{(3.3 \times 10^{-3} - 2x)^2} = 32$$

$$\Rightarrow \frac{x}{3.3 \times 10^{-3} - 2x} = 5.66$$

$$\Rightarrow x = 18.678 \times 10^{-3} - 11.32x$$

$$\Rightarrow 12.32x = 18.678 \times 10^{-3}$$

$$\Rightarrow x = 1.5 \times 10^{-3}$$

Therefore, at equilibrium,

$$[\text{BrCl}] = 3.3 \times 10^{-3} - (2 \times 1.5 \times 10^{-3})$$

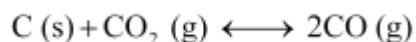
$$= 3.3 \times 10^{-3} - 3.0 \times 10^{-3}$$

$$= 0.3 \times 10^{-3}$$

$$= 3.0 \times 10^{-4} \text{ mol L}^{-1}$$

Question 7.23:

At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO₂ in equilibrium with solid carbon has 90.55% CO by mass



Calculate K_c for this reaction at the above temperature.

- **Answer**

Let the total mass of the gaseous mixture be 100 g.

Mass of CO = 90.55 g

And, mass of CO₂ = (100 – 90.55) = 9.45 g

$$\text{Now, number of moles of CO, } n_{\text{CO}} = \frac{90.55}{28} = 3.234 \text{ mol}$$

$$\text{Number of moles of CO}_2, n_{\text{CO}_2} = \frac{9.45}{44} = 0.215 \text{ mol}$$

Partial pressure of CO,

$$\begin{aligned}
 p_{\text{CO}} &= \frac{n_{\text{CO}}}{n_{\text{CO}} + n_{\text{CO}_2}} \times P_{\text{total}} \\
 &= \frac{3.234}{3.234 + 0.215} \times 1 \\
 &= 0.938 \text{ atm}
 \end{aligned}$$

Partial pressure of CO_2 ,

$$\begin{aligned}
 p_{\text{CO}_2} &= \frac{n_{\text{CO}_2}}{n_{\text{CO}} + n_{\text{CO}_2}} \times P_{\text{total}} \\
 &= \frac{0.215}{3.234 + 0.215} \times 1 \\
 &= 0.062 \text{ atm}
 \end{aligned}$$

$$\begin{aligned}
 \text{Therefore, } K_p &= \frac{[\text{CO}]^2}{[\text{CO}_2]} \\
 &= \frac{(0.938)^2}{0.062} \\
 &= 14.19
 \end{aligned}$$

For the given reaction,

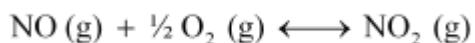
$$\Delta n = 2 - 1 = 1$$

We know that,

$$\begin{aligned}
 K_p &= K_c (RT)^{\Delta n} \\
 \Rightarrow 14.19 &= K_c (0.082 \times 1127)^1 \\
 \Rightarrow K_c &= \frac{14.19}{0.082 \times 1127} \\
 &= 0.154 \text{ (approximately)}
 \end{aligned}$$

Question 7.24:

Calculate a) ΔG^\bullet and b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298 K



where $\Delta_f G^\bullet (\text{NO}_2) = 52.0 \text{ kJ/mol}$

$\Delta_f G^\bullet (\text{NO}) = 87.0 \text{ kJ/mol}$

$\Delta_f G^\bullet (\text{O}_2) = 0 \text{ kJ/mol}$

- **Answer**

(a) For the given reaction,

$$\Delta G^\circ = 52.0 - \{87.0 + 0\}$$

$$= -35.0 \text{ kJ mol}^{-1}$$

(b) We know that,

$$\Delta G^\circ = RT \log K_c$$

$$\Delta G^\circ = 2.303 RT \log K_c$$

$$K_c = \frac{-35.0 \times 10^{-3}}{-2.303 \times 8.314 \times 298}$$
$$= 6.134$$

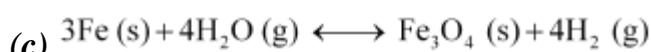
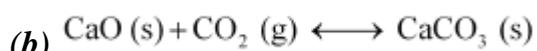
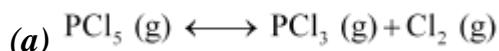
$$\therefore K_c = \text{antilog } (6.134)$$

$$= 1.36 \times 10^6$$

Hence, the equilibrium constant for the given reaction K_c is 1.36×10^6

Question 7.25:

Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?



• **Answer**

(a) The number of moles of reaction products will increase. According to Le Chatelier's principle, if pressure is decreased, then the equilibrium shifts in the direction in which the number of moles of gases is more. In the given reaction, the number of moles of gaseous products is more than that of gaseous reactants. Thus, the reaction will proceed in the forward direction. As a result, the number of moles of reaction products will increase.

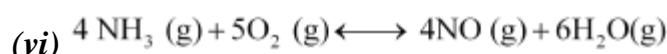
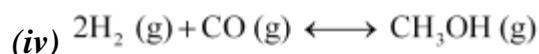
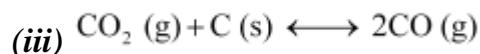
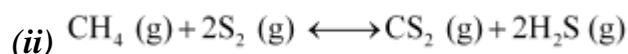
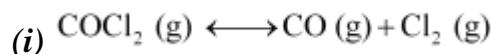
(b) The number of moles of reaction products will decrease.

(c) The number of moles of reaction products remains the same

Question 7.26:

Which of the following reactions will get affected by increasing the pressure?

Also, mention whether change will cause the reaction to go into forward or backward direction.



• **Answer**

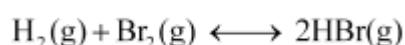
The reactions given in (i), (iii), (iv), (v), and (vi) will get affected by increasing the pressure.

The reaction given in (iv) will proceed in the forward direction because the number of moles of gaseous reactants is more than that of gaseous products.

The reactions given in (i), (iii), (v), and (vi) will shift in the backward direction because the number of moles of gaseous reactants is less than that of gaseous products.

Question 7.27:

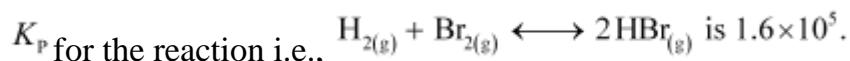
The equilibrium constant for the following reaction is 1.6×10^5 at 1024 K.



Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

• **Answer**

Given,



Therefore, for the reaction $2\text{HBr}_{(\text{g})} \rightleftharpoons \text{H}_{2(\text{g})} + \text{Br}_{2(\text{g})}$, the equilibrium constant will be,

$$K'_p = \frac{1}{K_p}$$

$$= \frac{1}{1.6 \times 10^5}$$

$$= 6.25 \times 10^{-6}$$

Now, let p be the pressure of both H_2 and Br_2 at equilibrium.

| | | | | | |
|----------------|----------------------------|-----------------------|--------------------------|---|---------------------------|
| | $2\text{HBr}_{(\text{g})}$ | \longleftrightarrow | $\text{H}_{2(\text{g})}$ | + | $\text{Br}_{2(\text{g})}$ |
| Initial conc. | 10 | | 0 | | 0 |
| At equilibrium | $10 - 2p$ | | p | | p |

Now, we can write,

$$\frac{P_{\text{HBr}} \times P_{\text{Br}_2}}{P_{\text{HBr}}^2} = K'_p$$

$$\frac{p \times p}{(10 - 2p)^2} = 6.25 \times 10^{-6}$$

$$\frac{p}{10 - 2p} = 2.5 \times 10^{-3}$$

$$p = 2.5 \times 10^{-2} - (5.0 \times 10^{-3})p$$

$$p + (5.0 \times 10^{-3})p = 2.5 \times 10^{-2}$$

$$(1005 \times 10^{-3})p = 2.5 \times 10^{-2}$$

$$p = 2.49 \times 10^{-2} \text{ bar} = 2.5 \times 10^{-2} \text{ bar (approximately)}$$

Therefore, at equilibrium,

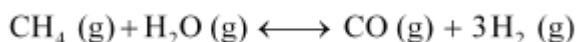
$$[\text{H}_2] = [\text{Br}_2] = 2.49 \times 10^{-2} \text{ bar}$$

$$[\text{HBr}] = 10 - 2 \times (2.49 \times 10^{-2}) \text{ bar}$$

$$= 9.95 \text{ bar} = 10 \text{ bar (approximately)}$$

Question 7.28:

Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:



(a) Write an expression for K_p for the above reaction.

(b) How will the values of K_p and composition of equilibrium mixture be affected by

- (i) Increasing the pressure**
- (ii) Increasing the temperature**
- (iii) Using a catalyst?**

• **Answer**

(a) For the given reaction,

$$K_p = \frac{P_{CO} \times P_{H_2}^3}{P_{CH_4} \times P_{H_2O}}$$

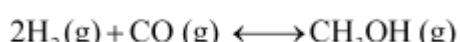
- (b)** (i) According to Le Chatelier's principle, the equilibrium will shift in the backward direction.
- (ii) According to Le Chatelier's principle, as the reaction is endothermic, the equilibrium will shift in the forward direction.
- (iii) The equilibrium of the reaction is not affected by the presence of a catalyst. A catalyst only increases the rate of a reaction. Thus, equilibrium will be attained quickly.

Question 7.29:

Describe the effect of:

- a) Addition of H_2**
- b) Addition of CH_3OH**
- c) Removal of CO**
- d) Removal of CH_3OH**

on the equilibrium of the reaction:

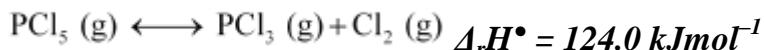


• **Answer**

- (a)** According to Le Chatelier's principle, on addition of H_2 , the equilibrium of the given reaction will shift in the forward direction.
- (b)** On addition of CH_3OH , the equilibrium will shift in the backward direction.
- (c)** On removing CO , the equilibrium will shift in the backward direction.
- (d)** On removing CH_3OH , the equilibrium will shift in the forward direction.

Question 7.30:

At 473 K, equilibrium constant K_c for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3} . If decomposition is depicted as,



- a) Write an expression for K_c for the reaction.
- b) What is the value of K_c for the reverse reaction at the same temperature?
- c) What would be the effect on K_c if (i) more PCl_5 is added (ii) pressure is increased? (iii) The temperature is increased?

• **Answer**

$$(a) \quad K_c = \frac{[\text{PCl}_3] [\text{Cl}_2]}{[\text{PCl}_5]}$$

(b) Value of K_c for the reverse reaction at the same temperature is:

$$\begin{aligned} K'_c &= \frac{1}{K_c} \\ &= \frac{1}{8.3 \times 10^{-3}} = 1.2048 \times 10^2 \\ &= 120 - 48 \end{aligned}$$

- (c) (i) K_c would remain the same because in this case, the temperature remains the same.
- (ii) K_c is constant at constant temperature. Thus, in this case, K_c would not change.
- (iii) In an endothermic reaction, the value of K_c increases with an increase in temperature. Since the given reaction is an endothermic reaction, the value of K_c will increase if the temperature is increased.

Question 7.31:

Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction

involves the formation of CO and H₂. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,



If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that $p_{\text{CO}} = p_{\text{H}_2\text{O}} = 4.0$ bar, what will be the partial pressure of H₂ at equilibrium? K_p = 10.1 at 400°C

• **Answer**

Let the partial pressure of both carbon dioxide and hydrogen gas be p . The given reaction is:

| | | | | | | |
|-------------------|-----------|----------------------------|----------------------|--------------------|-----|-------------------|
| $\text{CO}_{(g)}$ | + | $\text{H}_2\text{O}_{(g)}$ | \rightleftharpoons | $\text{CO}_{2(g)}$ | $+$ | $\text{H}_{2(g)}$ |
| Initial conc. | 4.0 bar | 4.0 bar | | 0 | 0 | |
| At equilibrium | $4.0 - p$ | $4.0 - p$ | | p | p | |

It is given that $K_p = 10.1$.

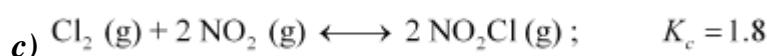
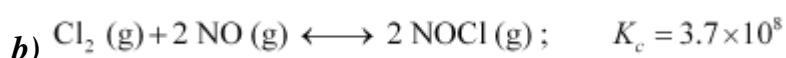
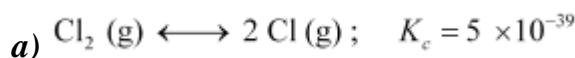
Now,

$$\begin{aligned} \frac{p_{\text{CO}_2} \times p_{\text{H}_2}}{p_{\text{CO}} \times p_{\text{H}_2\text{O}}} &= K_p \\ \Rightarrow \frac{p \times p}{(4.0 - p)(4.0 - p)} &= 10.1 \\ \Rightarrow \frac{p}{4.0 - p} &= 3.178 \\ \Rightarrow p &= 12.712 - 3.178p \\ \Rightarrow 4.178p &= 12.712 \\ \Rightarrow p &= 3.04 \end{aligned}$$

Hence, at equilibrium, the partial pressure of H₂ will be 3.04 bar.

Question 7.32:

Predict which of the following reaction will have appreciable concentration of reactants and products:



• **Answer**

If the value of K_c lies between 10^{-3} and 10^3 , a reaction has appreciable concentration of reactants and products. Thus, the reaction given in (c) will have appreciable concentration of reactants and products.

Question 7.33:

The value of K_c for the reaction



is 2.0×10^{-50} at $25^\circ C$. If the equilibrium concentration of O_2 in air at $25^\circ C$ is 1.6×10^{-2} , what is the concentration of O_3 ?

• **Answer**

The given reaction is:



$$\text{Then, } K_C = \frac{[O_{3(g)}]^2}{[O_{2(g)}]^3}$$

It is given that $K_C = 2.0 \times 10^{-50}$ and $[O_{2(g)}] = 1.6 \times 10^{-2}$.

Then, we have,

$$\begin{aligned} 2.0 \times 10^{-50} &= \frac{[O_{3(g)}]^2}{[1.6 \times 10^{-2}]^3} \\ \Rightarrow [O_{3(g)}]^2 &= 2.0 \times 10^{-50} \times (1.6 \times 10^{-2})^3 \\ \Rightarrow [O_{3(g)}]^2 &= 8.192 \times 10^{-56} \\ \Rightarrow [O_{3(g)}] &= 2.86 \times 10^{-28} \text{ M} \end{aligned}$$

Hence, the concentration of O_3 is 2.86×10^{-28} M.

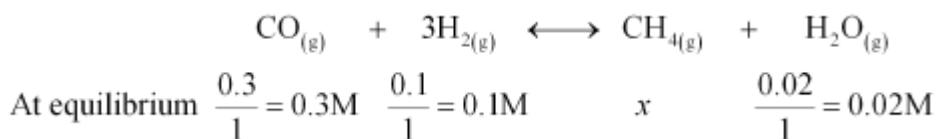
Question 7.34:

The reaction, $CO(g) + 3H_2(g) \longleftrightarrow CH_4(g) + H_2O(g)$ is at equilibrium at 1300 K in a 1L flask. It also contain 0.30 mol of CO , 0.10 mol of H_2 and 0.02 mol of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration

of CH_4 in the mixture. The equilibrium constant, K_c for the reaction at the given temperature is 3.90.

• **Answer**

Let the concentration of methane at equilibrium be x .



It is given that $K_c = 3.90$.

Therefore,

$$\begin{aligned} \frac{[\text{CH}_{4(\text{g})}][\text{H}_2\text{O}_{(\text{g})}]}{[\text{CO}_{(\text{g})}][\text{H}_{2(\text{g})}]^3} &= K_c \\ \Rightarrow \frac{x \times 0.02}{0.3 \times (0.1)^3} &= 3.90 \\ \Rightarrow x &= \frac{3.90 \times 0.3 \times (0.1)^3}{0.02} \\ &= \frac{0.00117}{0.02} \\ &= 0.0585\text{M} \\ &= 5.85 \times 10^{-2}\text{ M} \end{aligned}$$

Hence, the concentration of CH_4 at equilibrium is $5.85 \times 10^{-2}\text{ M}$.

Question 7.35:

What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species:



• **Answer**

A conjugate acid-base pair is a pair that differs only by one proton.

The conjugate acid-base for the given species is mentioned in the table below.

| Species | Conjugate acid-base |
|----------------|------------------------|
| HNO_2 | NO_2^- (base) |
| CN^- | HCN (acid) |

| | |
|--------------------|--|
| HClO_4 | ClO_4^- (base) |
| F^- | HF (acid) |
| OH^- | H_2O (acid) / O^{2-} (base) |
| CO_3^{2-} | HCO_3^- (acid) |
| S^{2-} | HS^- (acid) |

Question 7.36:

Which of the followings are Lewis acids? H_2O , BF_3 , H^+ , and NH_4^+

- **Answer**

Lewis acids are those acids which can accept a pair of electrons. For example, BF_3 , H^+ , and NH_4^+ are Lewis acids.

Question 7.37:

What will be the conjugate bases for the Brönsted acids: HF, H_2SO_4 and HCO_3^- ?

- **Answer**

The table below lists the conjugate bases for the given Bronsted acids.

| Bronsted acid | Conjugate base |
|-------------------------|--------------------|
| HF | F^- |
| H_2SO_4 | HSO_4^- |
| HCO_3^- | CO_3^{2-} |

Question 7.38:

Write the conjugate acids for the following Brönsted bases: NH_2^- , NH_3 and HCOO^- .

- **Answer**

The table below lists the conjugate acids for the given Bronsted bases.

| Bronsted base | Conjugate acid |
|-----------------|-----------------|
| NH_2^- | NH_3 |
| NH_3 | NH_4^+ |
| HCOO^- | HCOOH |

Question 7.39:

The species: H_2O , HCO_3^- , HSO_4^- , and NH_3 can act both as Brönsted acids and bases. For each case give the corresponding conjugate acid and base.

• **Answer**

The table below lists the conjugate acids and conjugate bases for the given species.

| Species | Conjugate acid | Conjugate base |
|-----------|----------------|----------------|
| H_2O | H_3O^+ | OH^- |
| HCO_3^- | H_2CO_3 | CO_3^{2-} |
| HSO_4^- | H_2SO_4 | SO_4^{2-} |
| NH_3 | NH_4^+ | NH_2^- |

Question 7.40:

Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base: (a) OH^- (b) F^- (c) H^+ (d) BCl_3 .

• **Answer**

- (a) OH^- is a Lewis base since it can donate its lone pair of electrons.
- (b) F^- is a Lewis base since it can donate a pair of electrons.
- (c) H^+ is a Lewis acid since it can accept a pair of electrons.
- (d) BCl_3 is a Lewis acid since it can accept a pair of electrons.

Question 7.41:

The concentration of hydrogen ion in a sample of soft drink is $3.8 \times 10^{-3} M$. what is its pH?

• **Answer**

Given,

$$[H^+] = 3.8 \times 10^{-3} M$$

\therefore pH value of soft drink

$$= -\log[H^+]$$

$$\begin{aligned}
&= -\log(3.8 \times 10^{-3}) \\
&= -\log 3.8 - \log 10^{-3} \\
&= -\log 3.8 + 3 \\
&= -0.58 + 3 \\
&= 2.42
\end{aligned}$$

Question 7.42:

The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

Question 7.43:

The ionization constant of HF, HCOOH and HCN at 298K are 6.8×10^{-4} , 1.8×10^{-4} and 4.8×10^{-9} respectively. Calculate the ionization constants of the corresponding conjugate base.

- **Answer**

It is known that,

$$K_b = \frac{K_w}{K_a}$$

Given,

$$K_a \text{ of HF} = 6.8 \times 10^{-4}$$

Hence, K_b of its conjugate base F^-

$$\begin{aligned}
&= \frac{K_w}{K_a} \\
&= \frac{10^{-14}}{6.8 \times 10^{-4}} \\
&= 1.5 \times 10^{-11}
\end{aligned}$$

Given,

$$K_a \text{ of HCOOH} = 1.8 \times 10^{-4}$$

Hence, K_b of its conjugate base HCOO^-

$$= \frac{K_w}{K_a}$$

$$= \frac{10^{-14}}{1.8 \times 10^{-4}} \\ = 5.6 \times 10^{-11}$$

Given,

$$K_a \text{ of HCN} = 4.8 \times 10^{-9}$$

Hence, K_b of its conjugate base CN^-

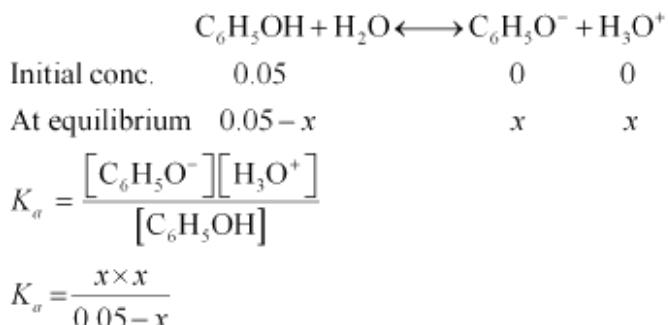
$$= \frac{K_w}{K_a} \\ = \frac{10^{-14}}{4.8 \times 10^{-9}} \\ = 2.08 \times 10^{-6}$$

Question 7.44:

The ionization constant of phenol is 1.0×10^{-10} . What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01M in sodium phenolate?

- **Answer**

Ionization of phenol:



As the value of the ionization constant is very less, x will be very small. Thus, we can ignore x in the denominator.

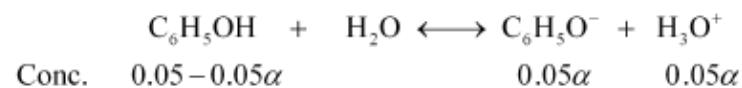
$$\therefore x = \sqrt{1 \times 10^{-10} \times 0.05} \\ = \sqrt{5 \times 10^{-12}} \\ = 2.2 \times 10^{-6} \text{ M} = [\text{H}_3\text{O}^+]$$

Since $[\text{H}_3\text{O}^+] = [\text{C}_6\text{H}_5\text{O}^-]$,
 $[\text{C}_6\text{H}_5\text{O}^-] = 2.2 \times 10^{-6} \text{ M}$.

Now, let α be the degree of ionization of phenol in the presence of 0.01 M C_6H_5ONa .



Also,



$$[C_6H_5OH] = 0.05 - 0.05\alpha ; 0.05 \text{ M}$$

$$[C_6H_5O^-] = 0.01 + 0.05\alpha ; 0.01 \text{ M}$$

$$[H_3O^+] = 0.05\alpha$$

$$K_a = \frac{[C_6H_5O^-][H_3O^+]}{[C_6H_5OH]}$$

$$K_a = \frac{(0.01)(0.05\alpha)}{0.05}$$

$$1.0 \times 10^{-10} = .01\alpha$$

$$\alpha = 1 \times 10^{-8}$$

Question 7.45:

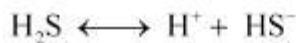
The first ionization constant of H_2S is 9.1×10^{-8} . Calculate the concentration of HS^- ion in its 0.1 M solution. How will this concentration be affected if the solution is 0.1 M in HCl also? If the second dissociation constant of H_2S is 1.2×10^{-13} , calculate the concentration of S^{2-} under both conditions.

- **Answer**

(i) To calculate the concentration of HS^- ion:

Case I (in the absence of HCl):

Let the concentration of HS^- be x M.



$$C_i \quad 0.1 \quad 0 \quad 0$$

$$C_f \quad 0.1-x \quad x \quad x$$

$$\text{Then, } K_{a_1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$9.1 \times 10^{-8} = \frac{(x)(x)}{0.1-x}$$

$$(9.1 \times 10^{-8})(0.1-x) = x^2$$

Taking $0.1-x \approx 0.1$ M ; 0.1M, we have $(9.1 \times 10^{-8})(0.1) = x^2$.

$$9.1 \times 10^{-8} = x^2$$

$$x = \sqrt{9.1 \times 10^{-8}}$$

$$= 9.54 \times 10^{-5} \text{ M}$$

$$\Rightarrow [\text{HS}^-] = 9.54 \times 10^{-5} \text{ M}$$

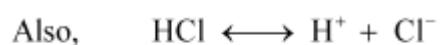
Case II (in the presence of HCl):

In the presence of 0.1 M of HCl, let $[\text{HS}^-]$ be y M.



$$C_i \quad 0.1 \quad 0 \quad 0$$

$$C_f \quad 0.1-y \quad y \quad y$$



$$0.1 \quad 0.1$$

$$\text{Now, } K_{a_1} = \frac{[\text{HS}^-][\text{H}^+]}{[\text{H}_2\text{S}]}$$

$$K_{a_1} = \frac{[y](0.1+y)}{(0.1-y)}$$

$$9.1 \times 10^{-8} = \frac{y \times 0.1}{0.1} \quad (\because 0.1 - y ; 0.1 \text{M})$$

(and $0.1 + y ; 0.1 \text{M}$)

$$9.1 \times 10^{-8} = y$$

$$\Rightarrow [\text{HS}^-] = 9.1 \times 10^{-8}$$

(ii) To calculate the concentration of $[\text{S}^{2-}]$:

Case I (in the absence of 0.1 M HCl):



$$[\text{HS}^-] = 9.54 \times 10^{-5} \text{ M} \quad (\text{From first ionization, case I})$$

Let $[\text{S}^{2-}]$ be X .

$$\text{Also, } [\text{H}^+] = 9.54 \times 10^{-5} \text{ M} \quad (\text{From first ionization, case I})$$

$$K_{a_2} = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]}$$

$$K_{a_2} = \frac{(9.54 \times 10^{-5})(X)}{9.54 \times 10^{-5}}$$

$$1.2 \times 10^{-13} = X = [\text{S}^{2-}]$$

Case II (in the presence of 0.1 M HCl):

Again, let the concentration of HS^- be X' M.

$$[\text{HS}^-] = 9.1 \times 10^{-8} \text{ M} \quad (\text{From first ionization, case II})$$

$$[\text{H}^+] = 0.1 \text{ M} \quad (\text{From HCl, case II})$$

$$[\text{S}^{2-}] = X'$$

$$\text{Then, } K_{a_2} = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]}$$

$$1.2 \times 10^{-13} = \frac{(0.1)(X')}{9.1 \times 10^{-8}}$$

$$10.92 \times 10^{-21} = 0.1X'$$

$$\frac{10.92 \times 10^{-21}}{0.1} = X'$$

$$X' = \frac{1.092 \times 10^{-20}}{0.1}$$

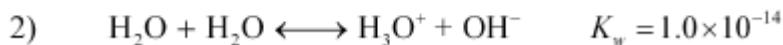
$$= 1.092 \times 10^{-19} \text{ M}$$

$$\Rightarrow K_{a_1} = 1.74 \times 10^{-5}$$

Question 7.46:

The ionization constant of acetic acid is 1.74×10^{-5} . Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.

- **Answer**



Degree of dissociation,

$$\alpha = \sqrt{\frac{K_a}{c}}$$

$$c = 0.05 \text{ M}$$

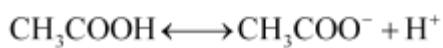
$$K_a = 1.74 \times 10^{-5}$$

$$\text{Then, } \alpha = \sqrt{\frac{1.74 \times 10^{-5}}{.05}}$$

$$\alpha = \sqrt{34.8 \times 10^{-5}}$$

$$\alpha = \sqrt{3.48} \times 10^{-4}$$

$$\alpha = 1.86 \times 10^{-2}$$



Thus, concentration of $\text{CH}_3\text{COO}^- = c \cdot \alpha$

$$= .05 \times 1.86 \times 10^{-2}$$

$$= .093 \times 10^{-2}$$

$$= .00093 \text{ M}$$

Since $[\text{oAc}^-] = [\text{H}^+]$,

$$[\text{H}^+] = .00093 = .093 \times 10^{-2}.$$

$$\text{pH} = -\log [\text{H}^+]$$

$$= -\log (.093 \times 10^{-2})$$

$$\therefore \text{pH} = 3.03$$

Hence, the concentration of acetate ion in the solution is 0.00093 M and its Ph is 3.03.

Question 7.47:

It has been found that the pH of a 0.01M solution of an organic acid is 4.15.

Calculate the concentration of the anion, the ionization constant of the acid and its pK_a .

• **Answer**

Let the organic acid be HA.



Concentration of HA = 0.01 M

pH = 4.15

$$-\log[\text{H}^+] = 4.15$$

$$[\text{H}^+] = 7.08 \times 10^{-5}$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Now,

$$[\text{H}^+] = [\text{A}^-] = 7.08 \times 10^{-5}$$

$$[\text{HA}] = 0.01$$

Then,

$$K_a = \frac{(7.08 \times 10^{-5})(7.08 \times 10^{-5})}{0.01}$$

$$K_a = 5.01 \times 10^{-7}$$

$$\begin{aligned} pK_a &= -\log K_a \\ &= -\log(5.01 \times 10^{-7}) \end{aligned}$$

$$pK_a = 6.3001$$

Question 7.48:

Assuming complete dissociation, calculate the pH of the following solutions:

- (a) 0.003 M HCl (b) 0.005 M NaOH (c) 0.002 M HBr (d) 0.002 M KOH

• **Answer**

(i) 0.003M HCl:



Since HCl is completely ionized,

$$[\text{H}_3\text{O}^+] = [\text{HCl}]$$

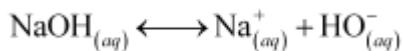
$$\Rightarrow [\text{H}_3\text{O}^+] = 0.003$$

Now,

$$\begin{aligned} \text{pH} &= -\log[\text{H}_3\text{O}^+] = -\log(0.003) \\ &= 2.52 \end{aligned}$$

Hence, the pH of the solution is 2.52.

(ii) 0.005M NaOH:



$$[\text{HO}^-] = [\text{NaOH}]$$

$$\Rightarrow [\text{HO}^-] = .005$$

$$\text{pOH} = -\log [\text{HO}^-] = -\log (.005)$$

$$\text{pOH} = 2.30$$

$$\therefore \text{pH} = 14 - 2.30$$

$$= 11.70$$

Hence, the pH of the solution is 11.70.

(iii) 0.002 HBr:



$$[\text{H}_3\text{O}^+] = [\text{HBr}]$$

$$\Rightarrow [\text{H}_3\text{O}^+] = .002$$

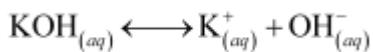
$$\therefore \text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$= -\log (0.002)$$

$$= 2.69$$

Hence, the pH of the solution is 2.69.

(iv) 0.002 M KOH:



$$[\text{OH}^-] = [\text{KOH}]$$

$$\Rightarrow [\text{OH}^-] = .002$$

$$\text{Now, } \text{pOH} = -\log [\text{OH}^-]$$

$$= 2.69$$

$$\therefore \text{pH} = 14 - 2.69$$

$$= 11.31$$

Hence, the pH of the solution is 11.31.

Question 7.49:

Calculate the pH of the following solutions:

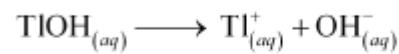
a) 2 g of TlOH dissolved in water to give 2 litre of solution.

- b) 0.3 g of $\text{Ca}(\text{OH})_2$ dissolved in water to give 500 mL of solution.**
- c) 0.3 g of NaOH dissolved in water to give 200 mL of solution.**
- d) 1mL of 13.6 M HCl is diluted with water to give 1 litre of solution.**

• **Answer**

(a) For 2g of TlOH dissolved in water to give 2 L of solution:

$$\begin{aligned}\left[\text{TlOH}_{(aq)} \right] &= \frac{2}{2} \text{g/L} \\ &= \frac{2}{2} \times \frac{1}{221} \text{M} \\ &= \frac{1}{221} \text{M}\end{aligned}$$



$$\left[\text{OH}_{(aq)}^- \right] = \left[\text{TlOH}_{(aq)} \right] = \frac{1}{221} \text{M}$$

$$K_w = [H^+] [OH^-]$$

$$10^{-14} = [H^+] \left(\frac{1}{221} \right)$$

$$221 \times 10^{-14} = [H^+]$$

$$\begin{aligned}\Rightarrow pH &= -\log[H^+] = -\log(221 \times 10^{-14}) \\ &= -\log(2.21 \times 10^{-12}) \\ &= 11.65\end{aligned}$$

(b) For 0.3 g of $\text{Ca}(\text{OH})_2$ dissolved in water to give 500 mL of solution:



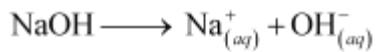
$$\left[\text{Ca(OH)}_2 \right] = 0.3 \times \frac{1000}{500} = 0.6 \text{M}$$

$$\begin{aligned}\left[\text{OH}_{aq}^- \right] &= 2 \times \left[\text{Ca(OH)}_{2aq} \right] = 2 \times 0.6 \\ &= 1.2 \text{M}\end{aligned}$$

$$\begin{aligned}\left[H^+ \right] &= \frac{K_w}{\left[OH_{aq}^- \right]} \\ &= \frac{10^{-14}}{1.2} \text{M} \\ &= 0.833 \times 10^{-14}\end{aligned}$$

$$\begin{aligned}
 \text{pH} &= -\log(0.833 \times 10^{-14}) \\
 &= -\log(8.33 \times 10^{-13}) \\
 &= (-0.902 + 13) \\
 &= 12.098
 \end{aligned}$$

(c) For 0.3 g of NaOH dissolved in water to give 200 mL of solution:



$$[\text{NaOH}] = 0.3 \times \frac{1000}{200} = 1.5 \text{ M}$$

$$[\text{OH}_{(\text{aq})}^-] = 1.5 \text{ M}$$

$$\begin{aligned}
 \text{Then, } [\text{H}^+] &= \frac{10^{-14}}{1.5} \\
 &= 6.66 \times 10^{-13}
 \end{aligned}$$

$$\begin{aligned}
 \text{pH} &= -\log(6.66 \times 10^{-13}) \\
 &= 12.18
 \end{aligned}$$

(d) For 1mL of 13.6 M HCl diluted with water to give 1 L of solution:

$$13.6 \times 1 \text{ mL} = M_2 \times 1000 \text{ mL}$$

(Before dilution) (After dilution)

$$13.6 \times 10^{-3} = M_2 \times 1 \text{ L}$$

$$M_2 = 1.36 \times 10^{-2}$$

$$[\text{H}^+] = 1.36 \times 10^{-2}$$

$$\text{pH} = -\log(1.36 \times 10^{-2})$$

$$= (-0.1335 + 2)$$

$$= 1.866 \square 1.8$$

Question 7.50:

The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK_a of bromoacetic acid.

- **Answer**

Degree of ionization, $\alpha = 0.132$

Concentration, $c = 0.1 \text{ M}$

Thus, the concentration of $\text{H}_3\text{O}^+ = c \cdot \alpha$

$$= 0.1 \times 0.132$$

$$= 0.0132$$

$$\begin{aligned}\text{pH} &= -\log [\text{H}^+] \\ &= -\log(0.0132) \\ &= 1.879 : 1.88\end{aligned}$$

Now,

$$\begin{aligned}K_a &= C\alpha^2 \\ &= 0.1 \times (0.132)^2\end{aligned}$$

$$K_a = .0017$$

$$pK_a = 2.75$$

Question 7.51:

The pH of 0.005M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate its ionization constant and pK_b .

• **Answer**

$$c = 0.005$$

$$\text{pH} = 9.95$$

$$\text{pOH} = 4.05$$

$$\text{pH} = -\log (4.105)$$

$$4.05 = -\log [\text{OH}^-]$$

$$[\text{OH}^-] = 8.91 \times 10^{-5}$$

$$c\alpha = 8.91 \times 10^{-5}$$

$$\alpha = \frac{8.91 \times 10^{-5}}{5 \times 10^{-3}} = 1.782 \times 10^{-2}$$

$$\text{Thus, } K_b = c\alpha^2$$

$$\begin{aligned}&= 0.005 \times (1.782)^2 \times 10^{-4} \\ &= 0.005 \times 3.1755 \times 10^{-4} \\ &= 0.0158 \times 10^{-4}\end{aligned}$$

$$K_b = 1.58 \times 10^{-6}$$

$$P_k_b = -\log K_b$$

$$\begin{aligned}&= -\log(1.58 \times 10^{-6}) \\ &= 5.80\end{aligned}$$

Question 7.52:

What is the pH of 0.001 M aniline solution? The ionization constant of aniline can be taken from Table 7.7. Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline.

• **Answer**

$$K_b = 4.27 \times 10^{-10}$$

$$c = 0.001\text{M}$$

$$\text{pH} = ?$$

$$\alpha = ?$$

$$k_b = c\alpha^2$$

$$4.27 \times 10^{-10} = 0.001 \times \alpha^2$$

$$4270 \times 10^{-10} = \alpha^2$$

$$65.34 \times 10^{-5} = \alpha = 6.53 \times 10^{-4}$$

$$\begin{aligned}\text{Then, } [\text{anion}] &= c\alpha = .001 \times 65.34 \times 10^{-5} \\ &= .065 \times 10^{-5}\end{aligned}$$

$$\begin{aligned}\text{pOH} &= -\log(.065 \times 10^{-5}) \\ &= 6.187\end{aligned}$$

$$\text{pH} = 7.813$$

Now,

$$K_a \times K_b = K_w$$

$$\therefore 4.27 \times 10^{-10} \times K_a = K_w$$

$$\begin{aligned}K_a &= \frac{10^{-14}}{4.27 \times 10^{-10}} \\ &= 2.34 \times 10^{-5}\end{aligned}$$

Thus, the ionization constant of the conjugate acid of aniline is 2.34×10^{-5} .

Question 7.53:

Calculate the degree of ionization of 0.05M acetic acid if its pK_a value is 4.74.

How is the degree of dissociation affected when its solution also contains (a) 0.01 M (b) 0.1 M in HCl?

• **Answer**

$$c = 0.05 \text{ M}$$

$$pK_a = 4.74$$

$$pK_a = -\log(K_a)$$

$$K_a = 1.82 \times 10^{-5}$$

$$K_a = c\alpha^2 \quad \alpha = \sqrt{\frac{K_a}{c}}$$

$$\alpha = \sqrt{\frac{1.82 \times 10^{-5}}{5 \times 10^{-2}}} = 1.908 \times 10^{-2}$$

When HCl is added to the solution, the concentration of H^+ ions will increase. Therefore, the equilibrium will shift in the backward direction i.e., dissociation of acetic acid will decrease.

Case I: When 0.01 M HCl is taken.

Let x be the amount of acetic acid dissociated after the addition of HCl.

| | CH_3COOH | \longleftrightarrow | H^+ | $+$ | CH_3COO^- |
|--------------------|--------------------------|-----------------------|--------------|-----|---------------------------|
| Initial conc. | 0.05 M | | 0 | | 0 |
| After dissociation | $0.05 - x$ | | $0.01 + x$ | | x |

As the dissociation of a very small amount of acetic acid will take place, the values i.e., $0.05 - x$ and $0.01 + x$ can be taken as 0.05 and 0.01 respectively.

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$\therefore K_a = \frac{(0.01)x}{0.05}$$

$$x = \frac{1.82 \times 10^{-5} \times 0.05}{0.01}$$

$$x = 1.82 \times 10^{-3} \times 0.05 \text{ M}$$

Now,

$$\alpha = \frac{\text{Amount of acid dissociated}}{\text{Amount of acid taken}}$$

$$= \frac{1.82 \times 10^{-3} \times 0.05}{0.05}$$

$$= 1.82 \times 10^{-3}$$

Case II: When 0.1 M HCl is taken.

Let the amount of acetic acid dissociated in this case be X . As we have done in the first case, the concentrations of various species involved in the reaction are:

$$[\text{CH}_3\text{COOH}] = 0.05 - X ; 0.05\text{M}$$

$$[\text{CH}_3\text{COO}^-] = X$$

$$[\text{H}^+] = 0.1 + X ; 0.1\text{M}$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$\therefore K_a = \frac{(0.1)X}{0.05}$$

$$x = \frac{1.82 \times 10^{-5} \times 0.05}{0.1}$$

$$x = 1.82 \times 10^{-4} \times 0.05\text{M}$$

Now,

$$\alpha = \frac{\text{Amount of acid dissociated}}{\text{Amount of acid taken}}$$

$$= \frac{1.82 \times 10^{-4} \times 0.05}{0.05}$$

$$= 1.82 \times 10^{-4}$$

Question 7.54:

The ionization constant of dimethylamine is 5.4×10^{-4} . Calculate its degree of ionization in its 0.02 M solution. What percentage of dimethylamine is ionized if the solution is also 0.1 M in NaOH?

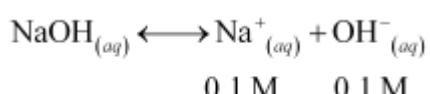
• Answer

$$K_b = 5.4 \times 10^{-4}$$

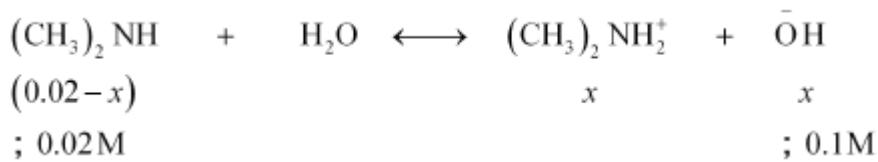
$$c = 0.02\text{ M}$$

$$\begin{aligned}\text{Then, } \alpha &= \sqrt{\frac{K_b}{c}} \\ &= \sqrt{\frac{5.4 \times 10^{-4}}{0.02}} \\ &= 0.1643\end{aligned}$$

Now, if 0.1 M of NaOH is added to the solution, then NaOH (being a strong base) undergoes complete ionization.



And,



$$\text{Then, } [(\text{CH}_3)_2\text{NH}_2^+] = x$$

$$[\text{OH}^-] = x + 0.1 ; 0.1$$

$$\Rightarrow K_b = \frac{[(\text{CH}_3)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}]}$$

$$5.4 \times 10^{-4} = \frac{x \times 0.1}{0.02}$$

$$x = 0.0054$$

It means that in the presence of 0.1 M NaOH, 0.54% of dimethylamine will get dissociated.

Question 7.55:

Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below:

- (a) **Human muscle-fluid, 6.83**
- (b) **Human stomach fluid, 1.2**
- (c) **Human blood, 7.38**
- (d) **Human saliva, 6.4.**

• **Answer**

(a) Human muscle fluid 6.83:

$$\text{pH} = 6.83$$

$$\text{pH} = -\log [\text{H}^+]$$

$$6.83 = -\log [\text{H}^+]$$

$$[\text{H}^+] = 1.48 \times 10^{-7} \text{ M}$$

(b) Human stomach fluid, 1.2:

$$\text{pH} = 1.2$$

$$1.2 = -\log [\text{H}^+]$$

$$[\text{H}^+] = 0.063$$

(c) Human blood, 7.38:

$$\text{pH} = 7.38 = -\log [\text{H}^+]$$

$$[\text{H}^+] = 4.17 \times 10^{-8} \text{ M}$$

(d) Human saliva, 6.4:

$$\text{pH} = 6.4$$

$$6.4 = -\log [\text{H}^+]$$

$$[\text{H}^+] = 3.98 \times 10^{-7}$$

Question 7.56:

The pH of milk, black coffee, tomato juice, lemon juice and egg white are 6.8, 5.0, 4.2, 2.2 and 7.8 respectively. Calculate corresponding hydrogen ion concentration in each.

• **Answer**

The hydrogen ion concentration in the given substances can be calculated by using the given relation:

$$\text{pH} = -\log [\text{H}^+]$$

(i) pH of milk = 6.8

$$\text{Since, pH} = -\log [\text{H}^+]$$

$$6.8 = -\log [\text{H}^+]$$

$$\log [\text{H}^+] = -6.8$$

$$[\text{H}^+] = \text{antilog}(-6.8)$$

$$= 1.5 \times 10^{-7} \text{ M}$$

(ii) pH of black coffee = 5.0

$$\text{Since, pH} = -\log [\text{H}^+]$$

$$5.0 = -\log [\text{H}^+]$$

$$\log [\text{H}^+] = -5.0$$

$$[\text{H}^+] = \text{antilog}(-5.0)$$

$$= 10^{-5} \text{ M}$$

(iii) pH of tomato juice = 4.2

$$\text{Since, pH} = -\log [\text{H}^+]$$

$$4.2 = -\log [\text{H}^+]$$

$$\log [\text{H}^+] = -4.2$$

$$[\text{H}^+] = \text{antilog}(-4.2)$$

$$= 6.31 \times 10^{-5} \text{ M}$$

(iv) pH of lemon juice = 2.2

$$\text{Since, } \text{pH} = -\log [\text{H}^+]$$

$$2.2 = -\log [\text{H}^+]$$

$$\log [\text{H}^+] = -2.2$$

$$[\text{H}^+] = \text{antilog}(-2.2)$$

$$= 6.31 \times 10^{-3} \text{ M}$$

(v) pH of egg white = 7.8

$$\text{Since, } \text{pH} = -\log [\text{H}^+]$$

$$7.8 = -\log [\text{H}^+]$$

$$\log [\text{H}^+] = -7.8$$

$$[\text{H}^+] = \text{antilog}(-7.8)$$

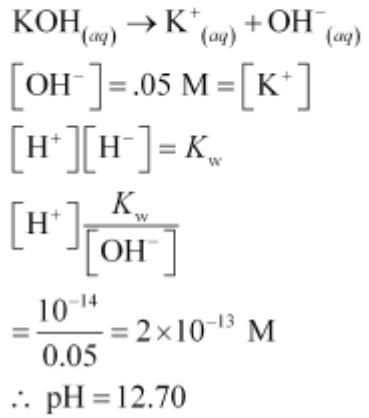
$$= 1.58 \times 10^{-8} \text{ M}$$

Question 7.57:

If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?

- **Answer**

$$\begin{aligned} [\text{KOH}_{aq}] &= \frac{0.561}{\frac{1}{5}} \text{ g/L} \\ &= 2.805 \text{ g/L} \\ &= 2.805 \times \frac{1}{56.11} \text{ M} \\ &= .05 \text{ M} \end{aligned}$$



Question 7.58:

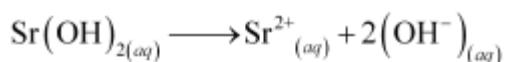
The solubility of Sr(OH)₂ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

• **Answer**

Solubility of Sr(OH)₂ = 19.23 g/L

Then, concentration of Sr(OH)₂

$$\begin{aligned} &= \frac{19.23}{121.63} \text{ M} \\ &= 0.1581 \text{ M} \end{aligned}$$



$$\therefore [\text{Sr}^{2+}] = 0.1581 \text{ M}$$

$$[\text{OH}^-] = 2 \times 0.1581 \text{ M} = 0.3126 \text{ M}$$

Now,

$$K_w = [\text{OH}^-] [\text{H}^+]$$

$$\frac{10^{-14}}{0.3126} = [\text{H}^+]$$

$$\Rightarrow [\text{H}^+] = 3.2 \times 10^{-14}$$

$$\therefore \text{pH} = 13.495 ; 13.50$$

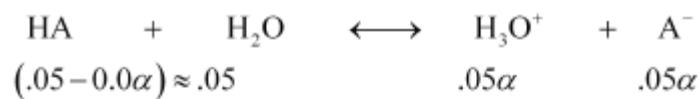
Question 7.59:

The ionization constant of propanoic acid is 1.32×10^{-5} . Calculate the degree of ionization of the acid in its 0.05M solution and also its pH. What will be its degree of ionization if the solution is 0.01M in HCl also?

• **Answer**

Let the degree of ionization of propanoic acid be α .

Then, representing propionic acid as HA, we have:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$
$$= \frac{(0.05\alpha)(0.05\alpha)}{0.05} = 0.05\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{0.05}} = 1.63 \times 10^{-2}$$

$$\text{Then, } [\text{H}_3\text{O}^+] = 0.05\alpha = 0.05 \times 1.63 \times 10^{-2} = K_b \cdot 1.5 \times 10^{-4} \text{ M}$$

$$\therefore \text{pH} = 3.09$$

In the presence of 0.1M of HCl, let α' be the degree of ionization.

$$\text{Then, } [\text{H}_3\text{O}^+] = 0.01$$

$$[\text{A}^-] = 0.005\alpha'$$

$$[\text{HA}] = 0.05$$

$$K_a = \frac{0.01 \times 0.05\alpha'}{0.05}$$

$$1.32 \times 10^{-5} = 0.01 \times \alpha'$$

$$\alpha' = 1.32 \times 10^{-3}$$

Question 7.60:

The pH of 0.1M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

• **Answer**

$$c = 0.1 \text{ M}$$

$$\text{pH} = 2.34$$

$$-\log[H^+] = \text{pH}$$

$$-\log[H^+] = 2.34$$

$$[H^+] = 4.5 \times 10^{-3}$$

Also,

$$[H^+] = c\alpha$$

$$4.5 \times 10^{-3} = 0.1 \times \alpha$$

$$\frac{4.5 \times 10^{-3}}{0.1} = \alpha$$

$$\alpha = 45 \times 10^{-3} = .045$$

Then,

$$\begin{aligned}K_a &= c\alpha^2 \\&= 0.1 \times (45 \times 10^{-3})^2 \\&= 202.5 \times 10^{-6} \\&= 2.02 \times 10^{-4}\end{aligned}$$

Question 7.61:

The ionization constant of nitrous acid is 4.5×10^{-4} . Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.

• **Answer**

NaNO₂ is the salt of a strong base (NaOH) and a weak acid (HNO₂).



$$K_h = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]}$$

$$\Rightarrow \frac{K_w}{K_a} = \frac{10^{-14}}{4.5 \times 10^{-4}} = .22 \times 10^{-10}$$

Now, If x moles of the salt undergo hydrolysis, then the concentration of various species present in the solution will be:

$$[\text{NO}_2^-] = .04 - x ; 0.04$$

$$[\text{HNO}_2] = x$$

$$[\text{OH}^-] = x$$

$$K_h = \frac{x^2}{0.04} = 0.22 \times 10^{-10}$$

$$x^2 = .0088 \times 10^{-10}$$

$$x = .093 \times 10^{-5}$$

$$\therefore [\text{OH}^-] = 0.093 \times 10^{-5} \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{10^{-14}}{.093 \times 10^{-5}} = 10.75 \times 10^{-9} \text{ M}$$

$$\Rightarrow \text{pH} = -\log(10.75 \times 10^{-9})$$

$$= 7.96$$

Therefore, degree of hydrolysis

$$= \frac{x}{0.04} = \frac{.093 \times 10^{-5}}{.04} = 2.325 \times 10^{-5}$$

Question 7.62:

A 0.02 M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine

- **Answer**

$$\text{pH} = 3.44$$

We know that,

$$\text{pH} = -\log [\text{H}^+]$$

$$\therefore [\text{H}^+] = 3.63 \times 10^{-4}$$

$$\text{Then, } K_h = \frac{(3.63 \times 10^{-4})^2}{0.02} \quad (\because \text{concentration} = 0.02 \text{ M})$$

$$\Rightarrow K_h = 6.6 \times 10^{-6}$$

$$\text{Now, } K_h = \frac{K_w}{K_a}$$

$$\Rightarrow K_a = \frac{K_w}{K_h} = \frac{10^{-14}}{6.6 \times 10^{-6}} \\ = 1.51 \times 10^{-9}$$

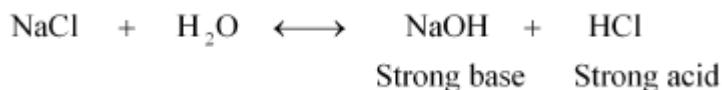
Question 7.63:

Predict if the solutions of the following salts are neutral, acidic or basic:

NaCl , KBr , NaCN , NH_4NO_3 , NaNO_2 and KF

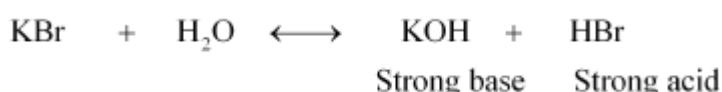
• **Answer**

(i) NaCl :



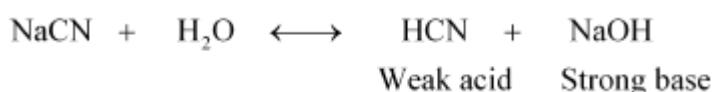
Therefore, it is a neutral solution.

(ii) KBr :



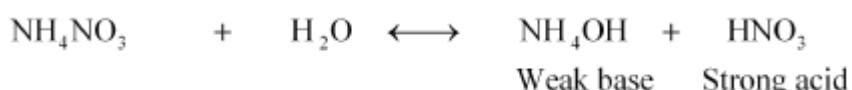
Therefore, it is a neutral solution.

(iii) NaCN :



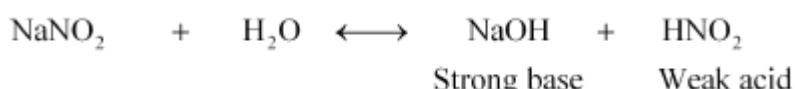
Therefore, it is a basic solution.

(iv) NH_4NO_3



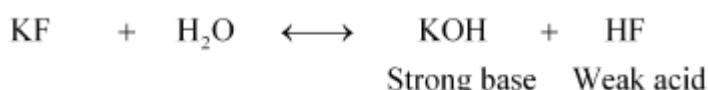
Therefore, it is an acidic solution.

(v) NaNO_2



Therefore, it is a basic solution.

(vi) KF



Therefore, it is a basic solution.

Question 7.64:

The ionization constant of chloroacetic acid is 1.35×10^{-3} . What will be the pH of 0.1M acid and its 0.1M sodium salt solution?

• **Answer**

It is given that K_a for ClCH_2COOH is 1.35×10^{-3} .

$$\Rightarrow K_a = c\alpha^2$$

$$\therefore \alpha = \sqrt{\frac{K_a}{c}}$$

$$= \sqrt{\frac{1.35 \times 10^{-3}}{0.1}} \quad (\because \text{concentration of acid} = 0.1\text{m})$$

$$\alpha = \sqrt{1.35 \times 10^{-2}}$$

$$= 0.116$$

$$\therefore [\text{H}^+] = c\alpha = 0.1 \times 0.116$$

$$= .0116$$

$$\Rightarrow \text{pH} = -\log[\text{H}^+] = 1.94$$

$\text{ClCH}_2\text{COONa}$ is the salt of a weak acid i.e., ClCH_2COOH and a strong base i.e., NaOH .



$$K_b = \frac{[\text{ClCH}_2\text{COOH}][\text{OH}^-]}{[\text{ClCH}_2\text{COO}^-]}$$

$$K_b = \frac{K_w}{K_a}$$

$$K_b = \frac{10^{-14}}{1.35 \times 10^{-3}} \\ = 0.740 \times 10^{-11}$$

$$\text{Also, } K_b = \frac{x^2}{0.1} \quad (\text{where } x \text{ is the concentration of OH}^- \text{ and ClCH}_2\text{COOH})$$

$$0.740 \times 10^{-11} = \frac{x^2}{0.1}$$

$$0.074 \times 10^{-11} = x^2$$

$$\Rightarrow x^2 = 0.74 \times 10^{-12}$$

$$x = 0.86 \times 10^{-6}$$

$$[\text{OH}^-] = 0.86 \times 10^{-6}$$

$$\therefore [\text{H}^+] = \frac{K_w}{0.86 \times 10^{-6}} \\ = \frac{10^{-14}}{0.86 \times 10^{-6}}$$

$$[\text{H}^+] = 1.162 \times 10^{-8}$$

$$\text{pH} = -\log [\text{H}^+] \\ = 7.94$$

Question 7.65:

Ionic product of water at 310 K is 2.7×10^{-14} . What is the pH of neutral water at this temperature?

- **Answer**

Ionic product,

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$\text{Let } [\text{H}^+] = x.$$

$$\text{Since } [\text{H}^+] = [\text{OH}^-], K_w = x^2.$$

$\Rightarrow K_w$ at 310K is 2.7×10^{-14} .

$$\therefore 2.7 \times 10^{-14} = x^2$$

$$\Rightarrow x = 1.64 \times 10^{-7}$$

$$\Rightarrow [\text{H}^+] = 1.64 \times 10^{-7}$$

$$\Rightarrow \text{pH} = -\log[\text{H}^+]$$

$$= -\log[1.64 \times 10^{-7}]$$

$$= 6.78$$

Hence, the pH of neutral water is 6.78.

Question 7.66:

Calculate the pH of the resultant mixtures:

a) 10 mL of 0.2M Ca(OH)_2 + 25 mL of 0.1M HCl

b) 10 mL of 0.01M H_2SO_4 + 10 mL of 0.01M Ca(OH)_2

c) 10 mL of 0.1M H_2SO_4 + 10 mL of 0.1M KOH

• **Answer**

(a) Moles of H_3O^+ = $\frac{25 \times 0.1}{1000} = .0025 \text{ mol}$

$$\text{Moles of } \text{OH}^- = \frac{10 \times 0.2 \times 2}{1000} = .0040 \text{ mol}$$

Thus, excess of $\text{OH}^- = .0015 \text{ mol}$

$$[\text{OH}^-] = \frac{.0015}{35 \times 10^{-3}} \text{ mol/L} = .0428$$

$$\text{pOH} = -\log[\text{OH}]$$

$$= 1.36$$

$$\text{pH} = 14 - 1.36$$

$$= 12.63 \quad (\text{not matched})$$

(b) Moles of H_3O^+ = $\frac{2 \times 10 \times 0.01}{1000} = .0002 \text{ mol}$

$$\text{Moles of } \text{OH}^- = \frac{2 \times 10 \times .01}{1000} = .0002 \text{ mol}$$

Since there is neither an excess of H_3O^+ or OH^- , the solution is neutral. Hence, pH = 7.

(c) Moles of $\text{H}_3\text{O}^+ = \frac{2 \times 10 \times 0.1}{1000} = .002 \text{ mol}$

$$\text{Moles of } \text{OH}^- = \frac{10 \times 0.1}{1000} = 0.001 \text{ mol}$$

$$\text{Excess of } \text{H}_3\text{O}^+ = .001 \text{ mol}$$

$$\text{Thus, } [\text{H}_3\text{O}^+] = \frac{.001}{20 \times 10^{-3}} = \frac{10^{-3}}{20 \times 10^{-3}} = .05$$

$$\therefore \text{pH} = -\log(0.05)$$

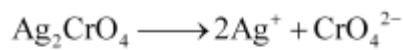
$$= 1.30$$

Question 7.67:

Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298K from their solubility product constants given in Table 7.9 (page 221). Determine also the molarities of individual ions.

• Answer

(1) Silver chromate:



Then,

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

Let the solubility of Ag_2CrO_4 be s.

$$\Rightarrow [\text{Ag}^+] 2s \text{ and } [\text{CrO}_4^{2-}] = s$$

Then,

$$K_{sp} = (2s)^2 \cdot s = 4s^3$$

$$\Rightarrow 1.1 \times 10^{-12} = 4s^3$$

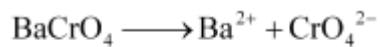
$$.275 \times 10^{-12} = s^3$$

$$s = 0.65 \times 10^{-4} \text{ M}$$

$$\text{Molarity of } \text{Ag}^+ = 2s = 2 \times 0.65 \times 10^{-4} = 1.30 \times 10^{-4} \text{ M}$$

Molarity of $\text{CrO}_4^{2-} = s = 0.65 \times 10^{-4} \text{ M}$

(2) Barium chromate:



$$\text{Then, } K_{sp} = [\text{Ba}^{2+}][\text{CrO}_4^{2-}]$$

Let s be the solubility of BaCrO_4 .

$$\text{Thus, } [\text{Ba}^{2+}] = s \text{ and } [\text{CrO}_4^{2-}] = s$$

$$\Rightarrow K_{sp} = s^2$$

$$\Rightarrow 1.2 \times 10^{-10} = s^2$$

$$\Rightarrow s = 1.09 \times 10^{-5} \text{ M}$$

Molarity of Ba^{2+} = Molarity of $\text{CrO}_4^{2-} = s = 1.09 \times 10^{-5} \text{ M}$

(3) Ferric hydroxide:



$$K_{sp} = [\text{Fe}^{3+}][\text{OH}^-]^3$$

Let s be the solubility of Fe(OH)_3 .

$$\text{Thus, } [\text{Fe}^{3+}] = s \text{ and } [\text{OH}^-] = 3s$$

$$\Rightarrow K_{sp} = s.(3s)^3$$

$$= s.27s^3$$

$$K_{sp} = 27s^4$$

$$1.0 \times 10^{-38} = 27s^4$$

$$.037 \times 10^{-38} = s^4$$

$$.00037 \times 10^{-36} = s^4 \quad \Rightarrow 1.39 \times 10^{-10} \text{ M} = S$$

Molarity of $\text{Fe}^{3+} = s = 1.39 \times 10^{-10} \text{ M}$

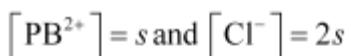
Molarity of $\text{OH}^- = 3s = 4.17 \times 10^{-10} \text{ M}$

(4) Lead chloride:



$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

Let K_{sp} be the solubility of PbCl_2 .



$$\text{Thus, } K_{sp} = s \cdot (2s)^2$$

$$= 4s^3$$

$$\Rightarrow 1.6 \times 10^{-5} = 4s^3$$

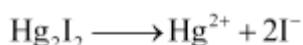
$$\Rightarrow 0.4 \times 10^{-5} = s^3$$

$$4 \times 10^{-6} = s^3 \Rightarrow 1.58 \times 10^{-2} \text{ M} = S.1$$

Molarity of $\text{PB}^{2+} = s = 1.58 \times 10^{-2} \text{ M}$

Molarity of chloride $= 2s = 3.16 \times 10^{-2} \text{ M}$

(5) Mercurous iodide:



$$K_{sp} = [\text{Hg}_2^{2+}]^2 [\text{I}^-]^2$$

Let s be the solubility of Hg_2I_2 .

$$\Rightarrow [\text{Hg}_2^{2+}] = s \text{ and } [\text{I}^-] = 2s$$

$$\text{Thus, } K_{sp} = s(2s)^2 \Rightarrow K_{sp} = 4s^3$$

$$4.5 \times 10^{-29} = 4s^3$$

$$1.125 \times 10^{-29} = s^3$$

$$\Rightarrow s = 2.24 \times 10^{-10} \text{ M}$$

Molarity of $\text{Hg}_2^{2+} = s = 2.24 \times 10^{-10} \text{ M}$

Molarity of $\text{I}^- = 2s = 4.48 \times 10^{-10} \text{ M}$

Question 7.68:

The solubility product constant of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.

• Answer

Let s be the solubility of Ag_2CrO_4 .

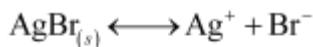


$$K_{sp} = (2s)^2 \cdot s = 4s^3$$

$$1.1 \times 10^{-12} = 4s^3$$

$$s = 6.5 \times 10^{-5} \text{ M}$$

Let s' be the solubility of AgBr.



$$K_{sp} = s'^2 = 5.0 \times 10^{-13}$$

$$\therefore s' = 7.07 \times 10^{-7} \text{ M}$$

Therefore, the ratio of the molarities of their saturated solution is

$$\frac{s}{s'} = \frac{6.5 \times 10^{-5} \text{ M}}{7.07 \times 10^{-7} \text{ M}} = 91.9.$$

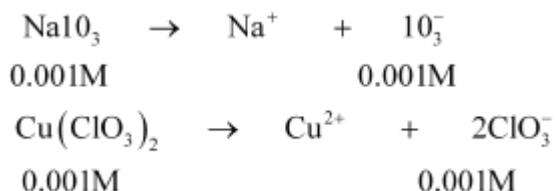
Question 7.69:

Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate? (For cupric iodate $K_{sp} = 7.4 \times 10^{-8}$).

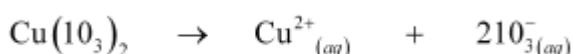
• **Answer**

When equal volumes of sodium iodate and cupric chlorate solutions are mixed together, then the molar concentrations of both solutions are reduced to half i.e., 0.001 M.

Then,



Now, the solubility equilibrium for copper iodate can be written as:



Ionic product of copper iodate:

$$\begin{aligned} &= [\text{Cu}^{2+}] [\text{IO}_3^-]^2 \\ &= (0.001)(0.001)^2 \\ &= 1 \times 10^{-9} \end{aligned}$$

Since the ionic product (1×10^{-9}) is less than K_{sp} (7.4×10^{-8}), precipitation will not occur.

Question 7.70:

The ionization constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13} . How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water?

• **Answer**

Since $\text{pH} = 3.19$,

$$[\text{H}_3\text{O}^+] = 6.46 \times 10^{-4} \text{ M}$$



$$K_a = \frac{[\text{C}_6\text{H}_5\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{COOH}]}$$

$$\frac{[\text{C}_6\text{H}_5\text{COOH}]}{[\text{C}_6\text{H}_5\text{COO}^-]} = \frac{[\text{H}_3\text{O}^+]}{K_a} = \frac{6.46 \times 10^{-4}}{6.46 \times 10^{-5}} = 10$$

Let the solubility of $\text{C}_6\text{H}_5\text{COOAg}$ be x mol/L.

Then,

$$[\text{Ag}^+] = x$$

$$[\text{C}_6\text{H}_5\text{COOH}] + [\text{C}_6\text{H}_5\text{COO}^-] = x$$

$$10[\text{C}_6\text{H}_5\text{COO}^-] + [\text{C}_6\text{H}_5\text{COO}^-] = x$$

$$[\text{C}_6\text{H}_5\text{COO}^-] = \frac{x}{11}$$

$$K_{sp} [\text{Ag}^+] [\text{C}_6\text{H}_5\text{COO}^-]$$

$$2.5 \times 10^{-13} = x \left(\frac{x}{11} \right)$$

$$x = 1.66 \times 10^{-6} \text{ mol/L}$$

Thus, the solubility of silver benzoate in a pH 3.19 solution is 1.66×10^{-6} mol/L.

Now, let the solubility of $\text{C}_6\text{H}_5\text{COOAg}$ be x' mol/L.

Then, $[\text{Ag}^+] = x' \text{ M}$ and $[\text{CH}_3\text{COO}^-] = x' \text{ M}$.

$$K_{sp} = [\text{Ag}^+] [\text{CH}_3\text{COO}^-]$$

$$K_{sp} = (x')^2$$

$$x' = \sqrt{K_{sp}} = \sqrt{2.5 \times 10^{-13}} = 5 \times 10^{-7} \text{ mol/L}$$

$$\therefore \frac{x}{x'} = \frac{1.66 \times 10^{-6}}{5 \times 10^{-7}} = 3.32$$

Hence, C_6H_5COOAg is approximately 3.317 times more soluble in a low pH solution.

Question 7.71:

What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide, $K_{sp} = 6.3 \times 10^{-18}$).

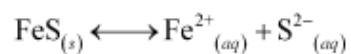
• **Answer**

Let the maximum concentration of each solution be x mol/L. After mixing, the volume of the concentrations of each solution will be

$$\therefore [FeSO_4] = [Na_2S] = \frac{x}{2} M \text{ reduced to half i.e., } \frac{x}{2}.$$

$$\text{Then, } [Fe^{2+}] = [FeSO_4] = \frac{x}{2} M$$

$$\text{Also, } [S^{2-}] = [Na_2S] = \frac{x}{2} M$$



$$K_{sp} = [Fe^{2+}][S^{2-}]$$

$$6.3 \times 10^{-18} = \left(\frac{x}{2}\right)\left(\frac{x}{2}\right)$$

$$\frac{x^2}{4} = 6.3 \times 10^{-18}$$

$$\Rightarrow x = 5.02 \times 10^{-9}$$

If the concentrations of both solutions are equal to or less than 5.02×10^{-9} M, then there will be no precipitation of iron sulphide

Question 7.72:

What is the minimum volume of water required to dissolve 1g of calcium sulphate at 298 K? (For calcium sulphate, K_{sp} is 9.1×10^{-6}).

• **Answer**



$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

Let the solubility of CaSO_4 be s .

$$\text{Then, } K_{sp} = s^2$$

$$9.1 \times 10^{-6} = s^2$$

$$s = 3.02 \times 10^{-3} \text{ mol/L}$$

Molecular mass of $\text{CaSO}_4 = 136 \text{ g/mol}$

Solubility of CaSO_4 in gram/L = $3.02 \times 10^{-3} \times 136$

$$= 0.41 \text{ g/L}$$

This means that we need 1L of water to dissolve 0.41g of CaSO_4

Therefore, to dissolve 1g of CaSO_4 we require $= \frac{1}{0.41} \text{ L} = 2.44 \text{ L}$ of water.

Question 7.73:

The concentration of sulphide ion in 0.1M HCl solution saturated with hydrogen sulphide is $1.0 \times 10^{-19} \text{ M}$. If 10 mL of this is added to 5 mL of 0.04 M solution of the following: FeSO_4 , MnCl_2 , ZnCl_2 and CdCl_2 . in which of these solutions precipitation will take place?

• **Answer**

Given K_{sp} for $\text{FeS} = 6.3 \times 10^{-18}$, $\text{MnS} = 2.5 \times 10^{-13}$, $\text{ZnS} = 1.6 \times 10^{-24}$,

$\text{CdS} = 8.0 \times 10^{-27}$

For precipitation to take place, it is required that the calculated ionic product exceeds the K_{sp} value.

Before mixing:

$$[\text{S}^{2-}] = 1.0 \times 10^{-19} \text{ M} \quad [\text{M}^{2+}] = 0.04 \text{ M}$$

$$\text{volume} = 10 \text{ mL} \quad \text{volume} = 5 \text{ mL}$$

After mixing:

$$[\text{S}^{2-}] = ? \quad [\text{M}^{2+}] = ?$$

volume = $(10 + 5) = 15 \text{ mL}$ volume = 15 mL

$$[\text{S}^{2-}] = \frac{1.0 \times 10^{-19} \times 10}{15} = 6.67 \times 10^{-20} \text{ M}$$

$$[\text{M}^{2+}] = \frac{0.04 \times 5}{15} = 1.33 \times 10^{-2} \text{ M}$$

$$\begin{aligned}\text{Ionic product} &= [\text{M}^{2+}][\text{S}^{2-}] \\ &= (1.33 \times 10^{-2})(6.67 \times 10^{-20}) \\ &= 8.87 \times 10^{-22}\end{aligned}$$

This ionic product exceeds the K_{sp} of ZnS and CdS. Therefore, precipitation will occur in CdCl₂ and ZnCl₂ solutions.

***** **THE END** *****