Some Basic Concepts of Chemistry

1

Introduction

Chemistry is the science of molecules and their transformations which deals with the study of matter, its composition, the changes that matter undergoes and the relation between changes in composition and changes in energy. Chemistry plays an important role in meeting human needs for food, health care products.

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.

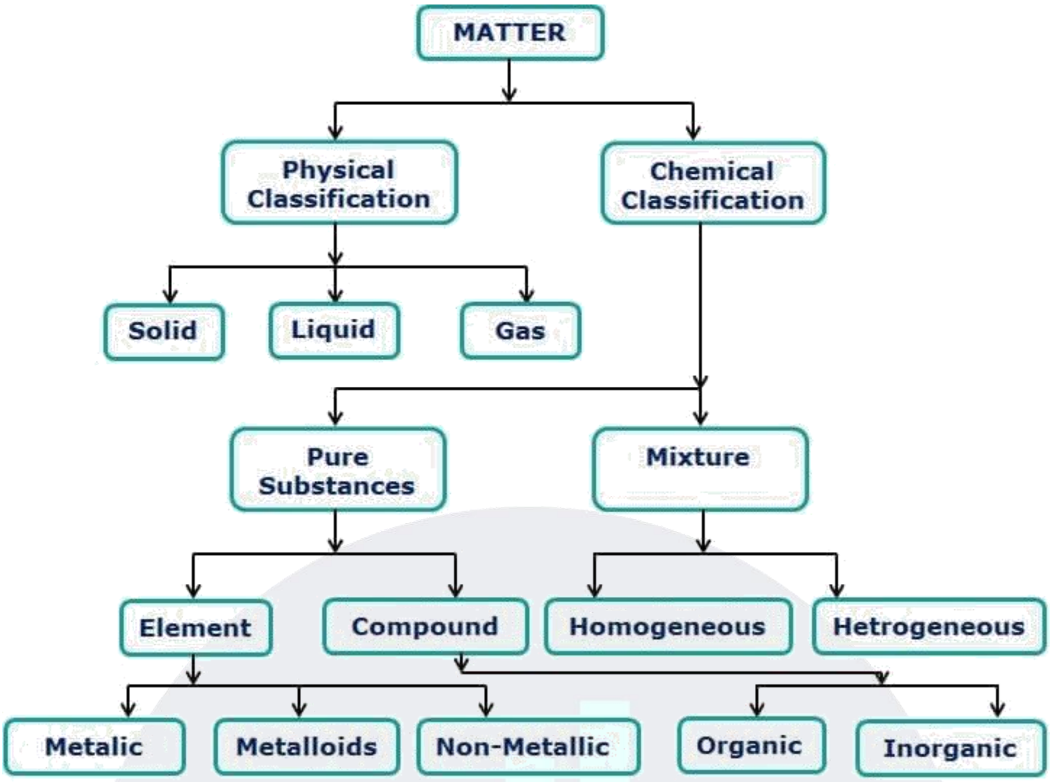
Importance of Chemistry:

Chemistry plays a central role in science and is often intertwined with other branches of science. Principles of chemistry are applicable in diverse areas, such as weather patterns, functioning of brain and operation of a computer, production in chemical industries, manufacturing fertilisers, alkalis, acids, salts, dyes, polymers, drugs, soaps, detergents, metals, alloys, etc., including new material.

Chemistry contributes in a big way to the national economy. It also plays an important role in meeting human needs for food, healthcare products and other material aimed at improving the quality of life.

Matter

Matter is anything that occupies space, has mass, offer resistance and can be perceived of directly by our senses. For example, book, pen, pencil, water, air, all living beings, etc.



(1) Physical classification

(a) Solid

(b) Liquid

(c) Gases

Solid	Liquid	Gases
(1) They have fixed shape and volume	They do not have fixed shape but have fixed volume	They do not have fixed shape and volume
(2) They cannot be compressed	They cannot be compressed	They can be compressed easily
(3) They have high density	They have moderate density	They have low density
(4) They do not flow	They flow easily	They flow easily
(5) They do not fill their container	They do not fill their container	They fill their container
(6) The forces of attraction are strong	The forces of attraction are less strong than solids	The forces of attraction are weak.
(7) Kinetic energy is least	Kinetic energy is more than solids	Kinetic energy is maximum.
(8) Particles are closely packed	Particles are not close as in solids	Particles are much farther apart from one another.
(9) For Example : Chair, table, chalk, book	For Ex: Water, petrol, cold drinks	For Ex: Oxygen, nitrogen, helium

Vapours represent a gaseous state of a substance which is liquid at room temperature.

A substance which is in gaseous state at room temperature is called a gas.

For Ex: Ammonia is a gas but on heating water forms vapours.

(2) Chemical classification

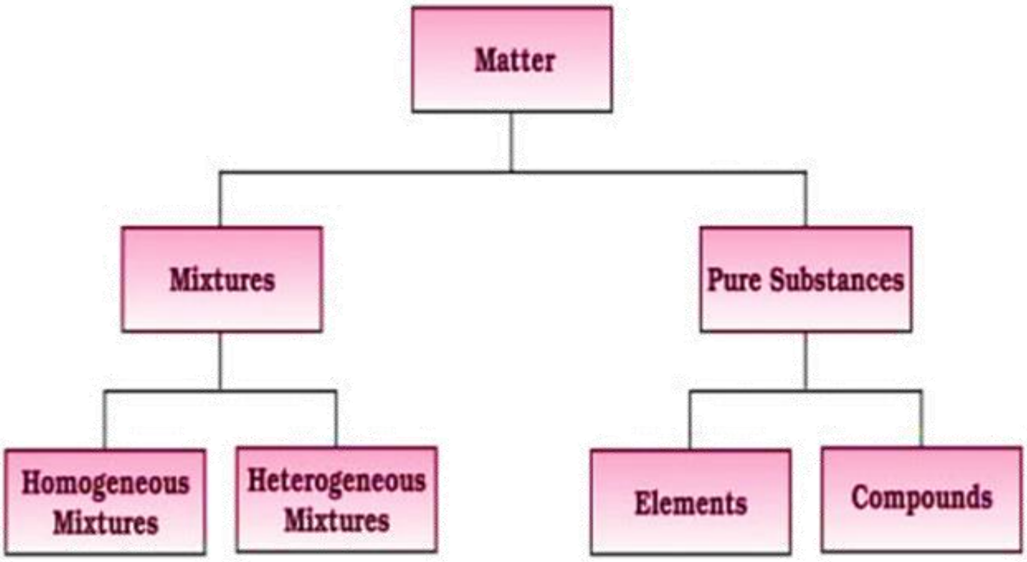
All kinds of matter are classified into two types:

(a) Homogeneous

(b) Heterogeneous

Material is said to be **homogeneous** if it has uniform composition and identical properties throughout Or a material is said to be homogeneous if it consist of only one phase.

A material is said to be **heterogeneous** if it consists of a number of phases. The different phases are separated from each other by distinct boundaries.



Element

Element is the purest form of matter. It is made up of only one type of atoms, ex.- carbon, iron, copper, oxygen etc.

Compound

Compound is the substance which is made up of two or more elements combined together in a fixed ratio by their weight e.g., carbon dioxide.

Mixture

Mixture is the substance which is made up of two or more substances in any ratio. e.g.,

Sugar + Water, Sodium Chloride + Water, Sand + Water

On the basis of composition, mixtures are of following type:

- **Homogeneous mixture**: The mixture which has uniform composition through out e.g., sugar solution.
- **Heterogeneous mixture**: The mixtures which do not have uniform composition through out. e.g. sand in water.

Atom

Atom is the smallest particle which may or may not exist free but takes part in chemical reaction. Atom word means not to be cut. Ex- H, Na, O etc.

International System of Units (S.I.)

The international system of units (in French Le Systeme International d' Unités - abbreviated as SI) was established in 1960 by the 11th general conference on weights and measures. SI system is a modification of metric system and has seven base units pertaining to the seven fundamental scientific quantities.

Base Physical Quantity	Symbol for Quantity	Name of SI Unit	Symbol for SI Unit
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Thermodynamic temperature	T	kelvin	K
Amount of substance	n	mole	mol
Luminous intensity	Iv	candela	cd

Prefixes in SI system

Multiple	Prefix	Symbol	Multiple	Prefix	Symbol
10^{-24}	yocto	y	10	deca	da
10^{-21}	zepto	z	10^{2}	hecto	h
10^{-18}	atto	a	10^{3}	kilo	k
10^{-15}	femto	f	10^{6}	mega	M
10^{-12}	pico	p	10^{9}	giga	G
10^{-9}	nano	n	10^{12}	tera	T
10^{-6}	micro	μ	10^{15}	peta	P
10^{-3}	milli	m	10^{18}	exa	E
10^{-2}	centi	c	10^{21}	zeta	Z
10^{-1}	deci	d	10^{24}	yotta	Y
10	deca	da			

Definition of SI Base Units

- **Metre**: The metre is the length of the path travelled by light in vacuum during a time interval of 1/(299792458) of a second.
- **Kilogram**: The kilogram is the unit of mass; it is equal to the mass of the international prototype of the kilogram.
- **Second**: The second is the duration of 9192631770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium-133 atom.
- **Ampere**: The ampere is that constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 metre apart in vacuum, would produce between these conductors a force equal to 2×10^{-7} newton per metre of length.
- **Kelvin**: The kelvin, unit of thermodynamic temperature, is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.
- **Mole**: 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”.
- **Candela**: The candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of 1/683 watt per steradian.

Uncertainty in Measurement

All scientific measurements involve certain degree of error or uncertainty. Scientific notations, significant figures and dimensional analysis help us in many ways in presenting of data and theoretical calculations.

Scientific Notation

It is an exponential 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. Thus, 232.508 can be written as 2.32508×10^2 in scientific notation.

Precision and Accuracy

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. Let the true value of a quantity is 3.9 and its measurements taken by two boys are 3.6 and 3.8. Here 3.8 is more accurate as it is closer to the true value. Similarly 3.85 is more precise than 3.9.

Significant Figures

i. The total number of digits in measuring of any physical quantity with certainty is called significant figures. There are certain rules for determining the number of significant figures.

ii. All digits are significant except zero in the beginning of a number. For example, in 285 cm, there are three significant figures.

iii. Zeros to the left of the first non-zero digit are not significant if such zeros follow the decimal point. For example, 0.03 has one significant figure.

iv. Zeros to the right of the decimal point are significant. For example, 0.200 g has three significant figures.

v. Zeros between two non-zero digits are significant. Thus, 2.005 has four significant figures.

vi. Counting the numbers of object, 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 zeroes after placing a decimal i.e., 2 = 2.000000 or 20 = 20.000000.

Notes: In additions or subtractions, the final result should be reported to the same number of decimal places as that of the term with the least number of decimal places.

Laws of Chemical Combination

All chemical reactions take place according to certain laws. These laws are known as laws of **chemical combination**.

i. **Law of conservation of mass**: This law was put forth by Antoine Lavoisier in 1789. According to this, "It states that the total mass of reactants is equal to the total mass of the products".

ii. **Law of constant composition:** This law was given by, a French chemist, Joseph Proust. This law states that a chemical compound is always found to be made of same elements combined together in fixed proportion by weight. CO_2 can be prepared by number of methods but always 12g carbon react with 32g of oxygen.

iii. **Law of multiple proportions**: This law was proposed by Dalton in 1803. According to this law, When two elements combine to form two or more chemical compounds, then weight of one of the element which combines with a fixed weight of the other, bears a simple whole number ratio to one another. This is called the law of multiple proportions.

For example, The ratio of masses of oxygen in CO and CO_2 for fixed mass of carbon (12) is 16 : 32 = 1 : 2.

iv. **Law of reciprocal proportions**: It states that the ratio of weights of two elements A and B, which combine separately with the fixed weight of a third element C is either same or some simple whole number of the ratio of weights in which A and B combine directly with each other.

For example, ratio of masses of carbon and sulphur which combine with the fixed mass (32 parts) of oxygen is 12 : 32 or 3 : 8.

v. **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 the same temperature and pressure.

For example, One volume of hydrogen and one volume of chlorine always combine to form two volumes of HCl gas.

vi. **Avogadro's Law**: In 1811, Avogadro proposed that equal volumes of all gases at the same temperature and pressure should contain equal number of molecules.

Dalton's Atomic Theory

John Dalton in 1808 published "A New System of Chemical Philosophy" in which he proposed atomic theory of matter. The main points of Dalton's atomic theory are as follows:

i. Matter is made up of extremely small, indivisible particles called atoms.

ii. Atoms of a given element are identical in all respect, i.e., they possess same size, shape, mass, chemical properties etc.

iii. Atoms of different elements are different in all respects, i.e., they possess different sizes, shapes, masses, chemical properties etc.

iv. Atoms of different elements may combine with each other in a fixed, simple, whole number ratio to form compounds.

v. Atoms can neither be created nor destroyed in a chemical reaction. Dalton's theory could explain the laws of chemical combination.

Atomic Mass and Molecular Mass

a) Atomic Mass: Atomic mass can be defined as a mass of a single atom which is measured in **atomic mass unit** (amu) or **unified mass** (u) where,

1 a.m.u. = $\frac{1}{12}$**th** of the mass of one C-12 atom

b) Molecular Mass: 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. **Molecular mass** expressed in grams is known as gram molecular mass.

Molecular mass of methane,

(CH_4) = (12.011 u) + 4 (1.008 u) = 16.043 u

The Mole

One mole is the amount of substance that contains as many as entities as number of atoms in exactly 12.00g of C-12.

Number of carbon atoms in 12 g of C-12 = 6.022×10^{23}

Chemical Formulae

Symbolic representation of compound is called chemical formula. It is of following types:

a) **Empirical Formula**: An **empirical formula** represents the simplest whole number ratio of various atoms present in a compound.

b) **Molecular Formula**: The molecular formula shows the exact number of different types of atoms present in a molecule of a compound.

Relationship between Empirical and Molecular Formula

Molecular formula = (Empirical formula) × n

Measurement of Concentration

The concentration of a solution reflects the relative proportion of solute and solvent present in the solution. The various concentration terms are,

1. **Weight percent** (% w/W) = (Weight of solute / Weight of solution) × 100.
2. **Volume percent** (% V/V) = (Volume of solute / Volume of solution) × 100.
3. **Molality (m)** – It is defined as number of moles of solute present in 1kg of solvent.

   m = {Number of moles of solute/Mass of solvent (in kg)} × 100.
4. **Molarity (M)** – It is defined as number of moles of solute present in 1 L of solution.

   M = {Number of moles of solute/Volume of solution (in litre)} × 100
5. **Mole fraction** : Suppose, n is the moles of solute and N is the moles of solvent, then,

   (i) Mole fraction of solute (X_{solute}) $= \frac{n}{n+N}$

   (ii) Mole fraction of solvent ($X_{solvent}$) $= \frac{N}{n+N}$

   $X_{solute} + X_{solvent} = 1$
6. **Normality**: It is defined as gram equivalent of solute dissolved in one litre solution.

$$N = \frac{\text{Gram equivalent of solute}}{\text{Volume of solution (litre)} \times 100}$$

Limiting Reagent

Limiting reagent is the reactant which is completely consumed in a reaction. To estimate the amount of product, limiting reagent should be known.

N_2(1 mole) + $3H_2$(3 mole) $\longrightarrow$ $2NH_3$(2 mole)

It means 1 mole of N_2 react with 3 mole of H_2 to produce 2 mole of NH_3.

You are here: Home / Class 11 / Chemistry / Some basic concepts of chemistry / Physical Quantities

Physical Quantities

Physical Properties

Physical Properties are those which can be measured or observed without changing the identity or composition of the substance.

For example : Mass, volume, melting point, boiling point.

Chemical properties

Chemical properties are those in which a chemical change in the substance occurs.

The measurement of any physical quantity consists of two parts:

(a) The number

(b) The unit

For example: If an object weighs 4.5 kg it involves two parts:

4.5 is the number and kg is the unit.

A unit is defined as the standard of reference chosen to measure any physical quantity.

French Academy of science in 1791 introduced a new system of measurement called metric system in which the different units of a physical quantity are related to each others as multiples of powers of 10.

For example: The improve System of units has been accepted internationally and is called International.

System of units or in short SI units (Systeme Internationale in French).

Seven base units

The seven basic physical quantities on which the international System of units is based, their symbols, the name of their units and the symbols of these units are given as:

Seven basic units

Measurement of Temperature

There are 3 scales of temperature:

(1) Degree Celsius

(2) Degree Fahrenheit

(3) Kelvin

The SI unit of Temperature is Kelvin

Relation between Degree kelvin and degree Celsius

Fahrenheit and Celsius relation

Relation between degree celsius and Degree Fahrenheit

Fahrenheit and Celsius relation

Measurement of Volume

The SI unit of volume is m^3

$1 \text{ L} = 1000 \text{ mL} = 1000 \text{ cm}^3$

$1 \text{ L} = 1 \text{ dm}^3$

$1 \text{ m}^3 = 100 \text{ (cm)}^3 = 10^3 \text{ L}$

Measurement of Mass

Mass is the quantity of matter contained in the sample and for the given sample it is constant and it does not depend upon the place.

weight is the force with with which the body is attracted towards the earth. It depends upon the acceleration due to gravity which varies from place to place. The mass of a substance can be determined very accurately in the laboratory by using analytical balance or electrical balance.

S.I. unit of mass is kilogram

1 Kg =1000 g

Units of Length

The S. I. unit of length is metre. It is also expressed in angstroms or nanometres or picometres.

Commonly used physical quantities and their derived units

Physical quantities and their derived units

Avogadro's hypothesis

Berzelius a Swedish chemist, gave a hypothesis called Berzelius hypothesis which states that :

Equal volume of all gases under similar conditions of temperature and pressure contain equal number of atoms.

For Example : Hydrogen + Chlorine ——————> 2 Hydrogen chloride gas

1 vol	1 vol	2 vol
n atoms	n atoms	2n molecule
On dividing throughout by 2n		
½ atom	½ atom	n molecules

This implies that one compound atom of hydrogen chloride is made up of ½ atom of hydrogen and ½ atom of chlorine. This is in direct conflict with Dalton's atomic theory which states that atoms are the ultimate particles of elements and are indivisible. This hypothesis was therefore rejected.

Avogadro's hypothesis

It states that equal volume of all gases under similar condition of temperature and pressure contain equal number of molecules .

Applications of Avogadro's law

1) In the calculation of atomicity of Elementary gases :

Atomicity of an elementary substance is defined as the number of atoms of the element present in 1 molecule of the substance.

For example : Atomicity of oxygen is 2 while that of ozone is 3.

Hydrogen	+ oxygen	————> Water Vapours
2n molecules	n molecules	2n molecules
On dividing throughout by 2n		
1 molecule	½ molecule	1 molecule

Thus one molecule of water contains ½ molecule of oxygen. But 1 molecule of water contains 1 atom of oxygen.

Hence ½ molecule = 1 molecule of oxygen

1 molecule of oxygen= 2 atoms of oxygen = 1 atom of oxygen= 2

2) To find the relationship between molecular mass and vapour density of a gas

Molecular mass = 2 × vapour density

3) To find the relationship between mass and volume of a gas 22.4 litres of any gas at STP weigh equal to the molecular mass of the gas expressed in grams. This is called gram molecular volume law.

Atomic and Molecular mass

As an atom is so small a particle that it cannot be seen or isolated ,therefore it is impossible to determine the actual mass of a single atom by weighing it.

The problem was finally solved by Avogadro's hypothesis. If equal volumes of two different gases are taken under similar conditions of temperature and pressure and then weighted, the ratio of their masses will be equal to the ratio of their single molecules. Thus, though the actual masses of the atoms could not be determined but their relative masses could be determined. If the atomic mass of the hydrogen is taken is 1 ,the relative atomic mass of oxygen is 16 .

Initially, the atomic masses of all the elements were obtained by comparing with the mass of hydrogen taken as 1 but by doing so, the atomic masses of most of the elements came out to be fractional.

Therefore carbon is taken reference for the determination of atomic masses.

Atomic mass of an element is the number of times an atom of that element is heavier than an atom of carbon taken as 12.

One atomic mass unit is equal to one twelfth of the mass of an atom of carbon 12 isotope.

The atomic mass of an element is the average relative mass of its atoms as compared with an atom of carbon 12 taken as 12.

Fractional abundance of an isotope is the fraction of the total number of atoms that is comprised of that particular isotope.

Fractional abundance

Gram Atomic mass

The atomic mass of an element expressed in grams is called gram atomic mass.

For Ex: Atomic mass of oxygen is 16 amu.

Gram atomic mass of oxygen = 16 g.

Molecular mass

The molecular mass of a substance is the number of times the molecule of the substance is heavier than one twelfth the mass of an atom of carbon -12.

or

The molecular mass is equal to sum of its atomic masses of all the atoms present in one molecule of substance.

For Example : Mass of H= 1 u

Atomic mass of O =16 u

Molecular mass of water =2 × atomic mass of H+1 × atomic mass of O

=2 × 1 + 16 × 1

= 18 u

Gram molecular mass

The molecular mass of a substance expressed in grams is called gram molecular mass.

For Example : Molecular mass of oxygen = 32u

Gram molecular mass of oxygen = 32 g

Mole Concept

1. Avogadro's number or Avogadro's constant (NA)
2. Mole
3. Importance of Avogadro's number and Mole Concept

Avogadro's number or Avogadro's constant (NA)

One gram atom of any element contains the same number of atoms and one gram molecule of any substance contains the same number of molecules.

The value was found to be 6.022137×10^{23}

The value generally used is 6.022×10^{23} .

This is called Avogadro's number or Avogadro's constant (NA)

Avogadro's number may be defined as the number of atoms present in one gram atom of the element or the number of molecules present in one gram molecule of the substance.

A mole is a chemist unit of counting particles such as atom, molecules, ions, electrons, protons which represent a value of 6.022×10^{23}

A mole of hydrogen atom means 6.022×10^{23} atoms of hydrogen whereas a mole of hydrogen molecule means 6.022×10^{23} molecules of hydrogen or $2 \times 6.022 \times 10^{23}$ atoms of hydrogen .

A mole of oxygen molecule means 6.022×10^{23} molecules of oxygen or $2 \times 6.022 \times 10^{23}$ atoms of oxygen.

A mole is defined as that amount of substance which has mass equal to gram atomic mass if the substance is atomic or gram molecular mass if the substance is molecular.

1 mole of carbon atoms =12 grams

1 mole of sodium atoms = 23 grams

1 mole of Oxygen atom = 16 grams

1 mole of Oxygen molecule = 32 grams

1 mole of water molecule = 18 grams

1 mole of carbon dioxide molecule = 44 grams

Mole

A mole is defined as that amount of substance which contains Avogadro's number of atoms if the substance is atomic or Avogadro's number of molecules if the substance is molecular.

1 mole of carbon atoms = 6.022 $\times 10^{23}$ atoms of carbon.

1 mole of sodium atom = 6.022 $\times 10^{23}$ atoms of sodium

1 mole of Oxygen atom = 6.022 $\times 10^{23}$ atoms of oxygen

1 mole of Oxygen molecule = 6.022 $\times 10^{23}$ molecules of oxygen

1 mole of water = 6.022 $\times 10^{23}$ molecules of water

In case of gases, a mole is defined as that amount of the gas which has a volume of 22.4 litres at STP.

1 mole of Oxygen gas = 22.4 litres of oxygen at STP

one mole of carbon dioxide gas = 22.4 litres of carbon dioxide at STP

A mole of an ionic compound is defined as that amount of the substance which has mass equal to gram formula mass or which contains Avogadro's number of formula unit.

1 mole of NaCl = 58.5 grams of NaCl

1 mole of NaCl = 6.022 $\times 10^{23}$ formula units of NaCl = 6.022 $\times 10^{23}$ Na+ ion and 6.022 $\times 10^{23}$ Cl– ion.

Importance of Avogadro's number and Mole Concept

In the calculation of actual mass of a single atom of an element or a single molecule of a substance.

In the calculation of the number of atoms or molecules in a given mass of the element of the compound.

In the calculation of the number of molecules present in a given volume of the gas under given conditions.

In the calculation of the size of the individual atoms and molecules assuming them to the spherical.

In the calculation of actual masses of 1 amu or 1 u.

1 amu = 1.6606 × 10^{-24} g

1 amu = 1.6606 × 10^{-27} kg

Empirical and Molecular Formula

Calculation of percentage composition

The percentage of any element or constituent in a compound is the number of parts by mass of that element or constituent present in 100 parts by mass of the compound.

Step 1 : Calculate the molecular mass of the compound from its formula by adding the atomic masses of the element present.

Step 2 : Calculate the percentage of elements or the constituents by applying the relation:

Percentage Composition

Question : Calculate the percentage of Carbon, Hydrogen and oxygen in Ethanol?

Answer :

$$\text{mass \% C} = \frac{24.022\text{ g}}{46.069\text{ g}} \times 100\ \% = 52.144\ \%$$

$$\text{Mass \% H} = \frac{6.048\text{ g}}{46.069\text{ g}} \times 100\ \% = 13.13\%$$

$$\text{Mass \% O} = \frac{15.999\text{ g}}{46.069\text{ g}} \times 100\ \% = 34.72\ \%$$

Empirical and Molecular Formula

The empirical formula of a compound is the chemical formula which expresses the simplest whole number ratio of the atoms of the various elements present in one molecule of the compound.

For Ex: The empirical formula of benzene is CH, hydrogen peroxide is HO, Glucose is CH2O.

The empirical formula represents only the atomic ratio of the various elements present in its molecule.

The molecular Formula of a compound is the chemical formula which represents the true formula of its molecules. It expresses the actual number of atoms of various elements present in one molecule of the compound.

The molecular formula of benzene is C6H6 , hydrogen peroxide is H2O2 , Glucose is C6H6.

Molecular Formula = n × Empirical formula

where n is any integer such as 1, 2, 3 ,4 etc.

The value of n can be obtained from the relation:

calculation of n

Molecular mass = 2 × Vapour Density

Calculation of Empirical Formula

Step 1 : Convert the mass percentage into grams.

Step 2 : Calculate the number of moles.

number of moles

Step 3 : Calculate the simplest molar ratio: Divide the moles obtained in step 1 by the smallest quotient or the least value from amongst the values obtained for each element.

Step 4 : Calculate the simplest whole number ratio.

Step 5 : Write the empirical formula.

Empirical Formula

The empirical Formula is C_2H_4O.

Calculation of molecular Formula

The molecular formula of a compound can de deduced from:

1) Empirical Formula

2) Molecular mass

Step 1: Calculation of the empirical formula from the percentage composition.

Step 2: Calculation of empirical formula mass by adding the atomic mass of all the atoms present in the empirical formula.

Step 3: Determination of the molecular mass of the compound from the given data.

Step 4: Determination of the value of n.

Step 5: Determination of the molecular formula

Question: 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 formula.

Answer:

Element	Symbol	Percentage Of element	Atomic mass	Moles of element	Simplest Molar ratio	Simplest Whole no. Molar ratio
Carbon	C	24.27	12	2.02	1	1
Hydrogen	H	4.07	1	4.07	2	2
Chlorine	Cl	71.65	35.5	2.02	1	1

The empirical formula of the compound is CH_2Cl

Empirical mass of $CH_2Cl = 12 + 2 \times 1 + 35.5 = 49.5$

n = 2

Molecular formula = n × E. F.

$= 2 \times CH_2Cl$

$= C_2H_4Cl_2$

Balancing of a Chemical Equation

Balancing of a chemical equation means making the number of atoms of each element equal on both sides of the equation.

The methods of balancing equation are:

1) Hit and Trial Method:

The simplest method to balance a chemical equation is by hit and trial method.

Step 1: Write down the correct formula of the reactants and products with plus sign in between with an arrow pointing from reactants to Products. This is called skeletal equation.

Step 2: Select the biggest formula from the Skeleton equation and equalise the number of atoms of each of its constituent elements on both sides of the chemical equation by suitable multiplication.

Step 3: When an elementary gas appears as a reactant or a product, the equation is balanced more easily by keeping the elementary gas in the atomic state. The balanced atomic equation is then made molecular by multiplying the whole equation by 2.

Question: Magnetic oxide when heated with hydrogen is reduced to iron and water is also produced. Write balanced equation for the reaction?

Answer: Magnetic oxide + Hydrogen ———-> Iron + Water

$Fe_3O_4 + H_2$ ——-> $Fe + H_2O$

To equalise the number of atoms of Fe on both sides, multiply Fe by 3 , we have

$Fe_3O_4 + H_2$ ——-> $3Fe + H_2O$

The above equation has 4 atoms of O on L.H.S. and 1 atoms of O on R.H.S.

To equalise, multiply water by 4.

$Fe_3O_4 + H_2$ ——-> $3Fe + 4H_2O$ ——-> 3Fe + 4H2O

The above equation has 8 H atoms on R.H.S. and 2 H atoms on L.H.S.

To equalise ,multiply H_2 on L.H.S. by 4

$Fe_3O_4 + 4H_2$ ——-> $3Fe + 4H_2O$

This a balanced chemical equation

2) Partial Equation method

Step 1 The chemical reaction represented by the equation is supposed to proceed in two or more steps.

Step 2 The Skeleton equation representing each step are written and then balanced by hit and trial method. These equations are known as partial equations.

Step 3 If necessary, the partial equation are multiplied by suitable integers so as to cancel those intermediate products which do not occur in the final reaction.

Step 4 The partial equations are added up to get the final balanced equation.

Question: The skeleton equation to represent the action of chlorine on a hot solution of sodium hydroxide is

$NaOH + Cl_2$ ————> $NaCl + NaClO_3 + H_2O$

Balance this equation by the method of partial equations

Answer: $Cl_2 + H_2O$ ———-> $H_2O + HClO$ + H_2O ———-> $H_2O + HClO$

$NaOH + HCl$ ————> $NaCl + H_2O$

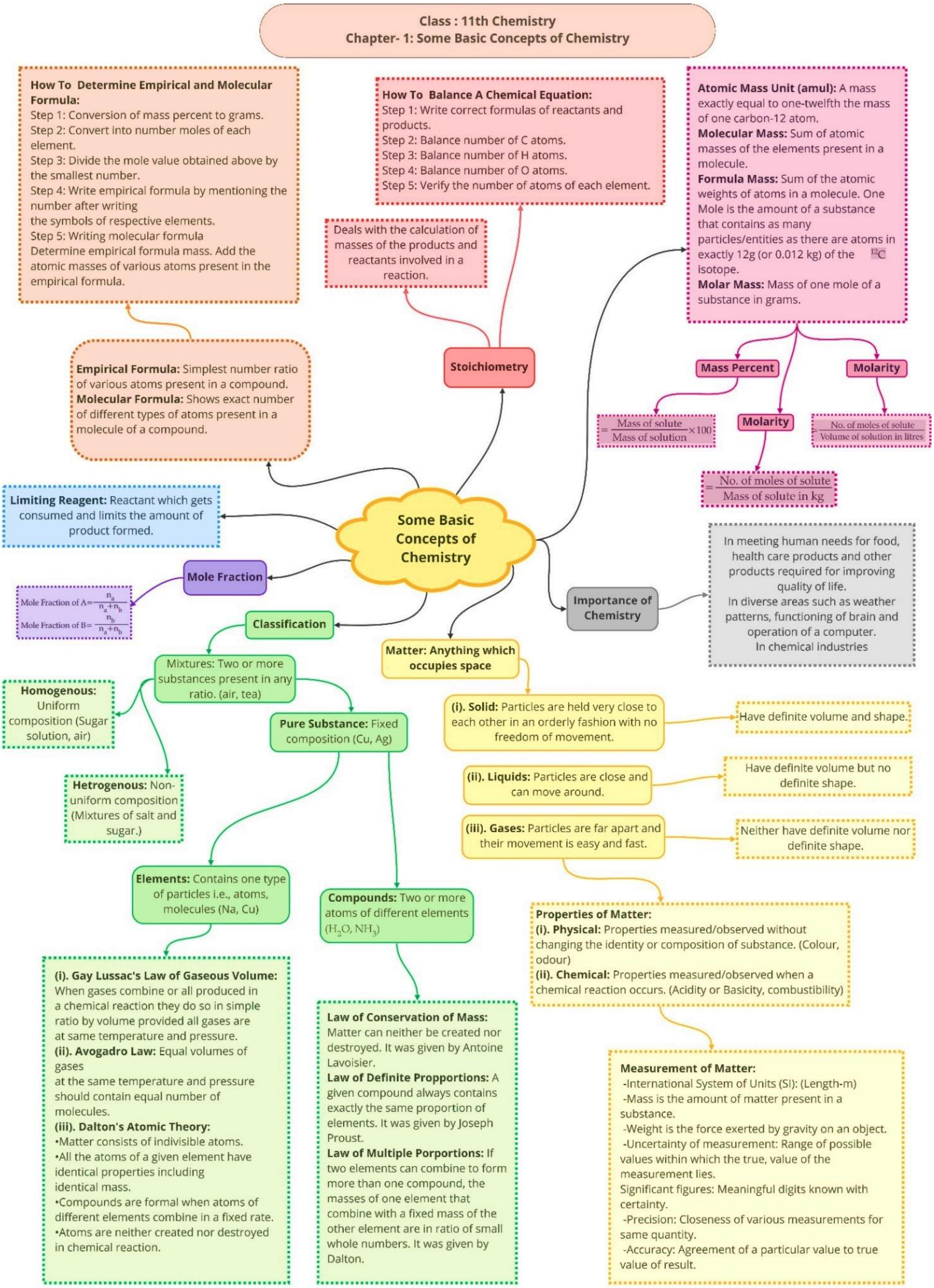
$NaOH + HClO$ ————> $NaClO + H_2O$

$3\ NaClO$ ———-> $2\ NaCl + NaClO_3$

$3\ Cl_2 + 6\ NaOH$ ————> $5\ NaCl + NaClO_3 + 3\ H_2O$

Summary

1. **Matter**: Anything that occupies space and has mass.
2. **Element**: A pure substance which can neither be decomposed into nor built from simpler substances by any physical or chemical method. It contains only one kind of atoms.
3. **Compound**: A pure substance which can be decomposed into simpler substances by some suitable chemical method. It contains only one kind of molecules.
4. **Mixture**: A substance obtained by simple mixing of two or more pure substances.
5. **Law of Conservation of Mass**: During any physical or chemical change total mass of the products formed is equal to the total mass of the reactants consumed.
6. **Law of Constant Composition**: A chemical compound always contains same elements combined together in same proportion of mass.
7. **Law of Multiple Proportions**: When two elements combine with each other to form two or more than two compounds then the masses of one of the elements that combine with the fixed mass of the other, bear a simple whole number ratio to one another.
8. **Gay Lussac's law**: When gases react with each other they do so in volumes which bear a simple whole number ratio to one another and to the volumes of products, if there are also gases, provided all volumes are measured under similar conditions of temperature and pressure.
9. **Avogadro's Law**: Equal volume of all gases under similar conditions contain equal number of molecules.
10. **Atom**: The smallest particle of an element that takes part in chemical reactions.
11. **Molecule**: The smallest particle of a substance that has independent existence.
12. **Atomicity**: The number of atoms in a molecule of the elementary substance.
13. **Unified Mass (u)**: One-twelfth of the actual mass of an atom of carbon (C-12). It is equal to 1.66×10^{-27} kg.
14. **Atomic Mass**: The average relative mass of an atom of the element as compared with mass of a carbon atom (C-12) taken as 12 u.
15. **Molecular Mass**: The average relative mass of a molecule of the substance as compared with mass of an atom of carbon (C-12) taken as 12 u.
16. **Gram Atomic Mass**: The mass of 1 mole of atoms (6×10^{23}) in g is called gram atomic mass.
17. **Gram Molecular Mass**: The mass of 1 gram molecule of compound expressed in grams.
18. **Avogadro's Number (NA)**: 6.022×10^{23}.
19. **Mole**: 6.022×10^{23} specified particles.
20. **Molar Mass**: Mass of one mole particles of the substance.
21. **Gram Molecular Volume (G.M.V.)**: Volume occupied by one mole molecules of the gaseous substance. Its value is equal to 22.4 L and S.T.P.
22. **Empirical Formula**: The formula which gives the simplest whole number ratio of atoms of different elements present in the molecule of the compound. Molecular formula is whole number multiple of empirical formula.
23. **Molarity (M)**: Number of moles of solute per litre of solution. Expressed as moles per litre or moles per dm3 or Molar (M).
24. Molarity changes with change in temperature because volume of the solution changes with change in temperature.
25. $K = {}^\circ C + 273.15$
26. ${}^\circ F = \frac{9}{5}({}^\circ C) + 32$



Class : 11th Chemistry
Chapter- 1: Some Basic Concepts of Chemistry

Some Basic Concepts of Chemistry

How To Determine Empirical and Molecular Formula:
Step 1: Conversion of mass percent to grams.
Step 2: Convert into number moles of each element.
Step 3: Divide the mole value obtained above by the smallest number.
Step 4: Write empirical formula by mentioning the number after writing the symbols of respective elements.
Step 5: Writing molecular formula
Determine empirical formula mass. Add the atomic masses of various atoms present in the empirical formula.

Empirical Formula: Simplest number ratio of various atoms present in a compound.
Molecular Formula: Shows exact number of different types of atoms present in a molecule of a compound.

Stoichiometry

Deals with the calculation of masses of the products and reactants involved in a reaction.

How To Balance A Chemical Equation:
Step 1: Write correct formulas of reactants and products.
Step 2: Balance number of C atoms.
Step 3: Balance number of H atoms.
Step 4: Balance number of O atoms.
Step 5: Verify the number of atoms of each element.

Atomic Mass Unit (amul): A mass exactly equal to one-twelfth the mass of one carbon-12 atom.
Molecular Mass: Sum of atomic masses of the elements present in a molecule.
Formula Mass: Sum of the atomic weights of atoms in a molecule. One Mole is the amount of a substance that contains as many particles/entities as there are atoms in exactly 12g (or 0.012 kg) of the ^{12}C isotope.
Molar Mass: Mass of one mole of a substance in grams.

Mass Percent

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

Molarity

$= \frac{\text{No. of moles of solute}}{\text{Mass of solute in kg}}$

Molarity

$= \frac{\text{No. of moles of solute}}{\text{Volume of solution in litres}}$

Limiting Reagent: Reactant which gets consumed and limits the amount of product formed.

Mole Fraction

$\text{Mole Fraction of A} = \frac{n_a}{n_a + n_b}$

$\text{Mole Fraction of B} = \frac{n_b}{n_a + n_b}$

Importance of Chemistry

In meeting human needs for food, health care products and other products required for improving quality of life.
In diverse areas such as weather patterns, functioning of brain and operation of a computer.
In chemical industries

Classification

Mixtures: Two or more substances present in any ratio. (air, tea)

Homogenous: Uniform composition (Sugar solution, air)

Hetrogenous: Non-uniform composition (Mixtures of salt and sugar.)

Pure Substance: Fixed composition (Cu, Ag)

Elements: Contains one type of particles i.e., atoms, molecules (Na, Cu)

Compounds: Two or more atoms of different elements (H_2O, NH_3)

(i). Gay Lussac's Law of Gaseous Volume: When gases combine or all produced in a chemical reaction they do so in simple ratio by volume provided all gases are at same temperature and pressure.
(ii). Avogadro Law: Equal volumes of gases at the same temperature and pressure should contain equal number of molecules.
(iii). Dalton's Atomic Theory:
•Matter consists of indivisible atoms.
•All the atoms of a given element have identical properties including identical mass.
•Compounds are formal when atoms of different elements combine in a fixed rate.
•Atoms are neither created nor destroyed in chemical reaction.

Law of Conservation of Mass: Matter can neither be created nor destroyed. It was given by Antoine Lavoisier.
Law of Definite Propportions: A given compound always contains exactly the same proportion of elements. It was given by Joseph Proust.
Law of Multiple Porportions: 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 ratio of small whole numbers. It was given by Dalton.

Matter: Anything which occupies space

(i). Solid: Particles are held very close to each other in an orderly fashion with no freedom of movement.
Have definite volume and shape.

(ii). Liquids: Particles are close and can move around.
Have definite volume but no definite shape.

(iii). Gases: Particles are far apart and their movement is easy and fast.
Neither have definite volume nor definite shape.

Properties of Matter:
(i). Physical: Properties measured/observed without changing the identity or composition of substance. (Colour, odour)
(ii). Chemical: Properties measured/observed when a chemical reaction occurs. (Acidity or Basicity, combustibility)

Measurement of Matter:
-International System of Units (SI): (Length-m)
-Mass is the amount of matter present in a substance.
-Weight is the force exerted by gravity on an object.
-Uncertainty of measurement: Range of possible values within which the true, value of the measurement lies.
Significant figures: Meaningful digits known with certainty.
-Precision: Closeness of various measurements for same quantity.
-Accuracy: Agreement of a particular value to true value of result.

Important Questions

Multiple Choice Questions

1. Formula of Ferric Sulphate is:
   (a) $FeSo_4$
   (b) $Fe\ (So_4)_3$
   (c) $Fe_2\ (So_4)_3$
   (d) Fe_2So_4

2. Approximate atomic weight of an element is 26.89. If its equivalent weight is 8.9, the exact atomic weight of element would be
   (a) 26.89
   (b) 8.9
   (c) 17.8
   (d) 26.7

3. The total number of atoms represented by the compound $CuSO_4 . 5H_2O$ is
   (a) 27
   (b) 21
   (c) 5
   (d) 8

4. An atom is 10 times heavier than 1/12th of mass of a carbon atom (C – 12). The mass of the atom in a.m.u. is
   (a) 10
   (b) 120
   (c) 1.2
   (d) 12

5. 81.4 g sample of ethyl alcohol contains 0.002 g of water. The amount of pure ethyl alcohol to the proper number of significant figures is
   (a) 81.398 g
   (b) 71.40 g
   (c) 91.4 g
   (d) 81 g

6. Which of the following halogen can be purified by sublimation?
   (a) F_2
   (b) Cl_2
   (c) Br_2
   (d) I_2

7. 1 mol of CH_4 contains
   (a) 6.02×10^{23} atoms of H
   (b) 4 g atom of Hydrogen
   (c) 1.81×10^{23} molecules of CH_4
   (d) 3.0 g of carbon

8. The prefix zepto stands for
   (a) 10_9
   (b) 10^{-12}
   (c) 10^{-15}
   (d) 10^{-21}

9. Which has maximum number of atoms?
   (a) 24 g of C (12)
   (b) 56 g of Fe (56)
   (c) 27 gof Al (27)
   (d) 108 g of Ag (108)

10: Irrespective of the source, pure sample, of water always yields 88.89% mass of oxygen and 11.11% mass of hydrogen. This is explained by the law of
   (a) Conservation of Mass
   (b) Multiple Proportions
   (c) Constant Composition
   (d) Constant Volume

11. Hemoglobin contains 0.33% of iron by weight. The molecular weight of hemoglobin is approximately 67200. The number of iron atoms (At. wt. of Fe = 56) present in one molecule of hemoglobin is
   (a) 6
   (b) 1
   (c) 4
   (d) 2

12. The -ve charged particles is called:
   (a) Anion
   (b) Cation
   (c) Radical
   (d) Atom

13. Which of the following contains same number of carbon atoms as are in 6.0 g of carbon (C – 12)?
   (a) 6.0 g Ethane
   (b) 8.0 g Methane
   (c) 21.0 g Propane
   (d) 28.0 g CO

14. The density of a gas is 1.78 gL^{-1} at STP. The weight of one mole of gas is
    (a) 39.9 g
    (b) 22.4 g
    (c) 3.56 g
    (d) 29 g
15. Molarity of 0.2 N H_2SO_4 is
    (a) 0.2
    (b) 0.4
    (c) 0.6
    (d) 0.1

Very Short:

1. What is chemistry?
2. How has chemistry contributed towards nation's development?
3. Differentiate solids, liquids & gases in terms of volume & shapes.
4. Name the different methods that can be used for separation of components of a mixture.
5. Classify following as pure substances and mixtures – Air, glucose, gold, odium and milk
6. What is the difference between molecules and compounds? Give examples of each.?
7. How can we separate the components of a compound?
8. How are physical properties different from chemical properties?
9. What are the two different system of measurement?
10. What is the SI unit of density?

Short Questions:

1. Define Mole. What is its numerical value?
2. Define molarity. Is it affected by a change in temperature?
3. What do you mean by Precision and accuracy?
4. Distinguish between fundamental and the derived units.
5. Define molality and write its temperature dependence.
6. Distinguish between an atom and a molecule.
7. Derive the SI unit of Joule (J) in terms of fundamental units.

Long Questions:

1. State the law of Multiple Proportions. Explain with two examples.
2. State the law of Constant Composition. Illustrate with two examples.
3. Define empirical formula and molecular formula. How will you establish a relationship between the two? Give examples.
4. In the commercial manufacture of nitric acid, how many moles of NO2 produce 7.33 mol HN03 in the reaction

   $3\ NO_2(g) + H_2O(1) \rightarrow 2HNO_3(aq) + NO(g)$
5. A sample of $NaNO_3$ weighing 0.83 g is placed in a 50,0 mL volumetric flask. The flask is then filled with water upon the etched mark. What is the molarity of the solution?

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A) : The empirical mass of ethene is half of its molecular mass.

   Reason (R) : The empirical formula represents the simplest whole-number ratio of various atoms present in a compound.

   (i) Both A and R are true and R is the correct explanation of A.
   (ii) A is true but R is false.
   (iii) A is false but R is true.
   (iv) Both A and R are false.
2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A) : One atomic mass unit is defined as one twelfth of the mass of one carbon-12 atom.

   Reason (R) : Carbon-12 isotope is the most abundant isotope of carbon and has been chosen as standard.

   (i) Both A and R are true and R is the correct explanation of A.
   (ii) Both A and R are true but R is not the correct explanation of A.
   (iii) A is true but R is false.
   (iv) Both A and R are false.

Case Study Based Question:

1. Chemistry is the science of molecules and their transformations. It is the science not so much of the one hundred elements but of the infinite variety of molecules that may be built from them. Chemistry plays a central role in science and is often intertwined with other branches ofscience.to understand the basic concepts of chemistry, which begin with the concept of matter. Let us start with the nature of matter. matter can exist in three physical states viz. solid, liquid and gas. Particles are held very close to each other in solids 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. different states of matter exhibit the following characteristics:

   I. Solids have definite volume and definite shape.

   II. Liquids have definite volume but do not have definite shape. They take the shape of the container in which they are placed.

   III. Gases have neither definite volume nor definite shape. They completely occupy the space in the container in which they are placed.

   Matter can be classified as mixture or pure substance. A mixture may be homogeneous or heterogeneous. Pure substances can further be classified into elements and compounds. Particles of an element consist of only one type of atoms. These particles may exist as atoms or molecules. When two or more atoms of different elements combine together in a definite ratio, the molecule of a compound is obtained.

   Every substance has unique or characteristic properties. These properties can be classified into two categories — physical properties, such as colour, odour, melting point, boiling point, density, etc., and chemical properties, like composition, combustibility, reactivity with acids and bases, etc. Physical properties can be measured or observed without changing the identity or the composition of the substance. The measurement or observation of chemical properties requires a chemical change to occur. Measurement of physical properties does not require occurrence of a chemical change.

   (1) Which of the following state of matter have definite volume but do not have definite shape ?

   (a) Solid

   (b) Liquid

   (c) Gas

   (d) Plasma

   (2) Particles are held very close to each other in ... in an orderly fashion and there is not much freedom of movement.

   (a) Liquid

   (b) Gas

   (c) Solid

   (d) Plasma

   (3) Particles of .... consist of only one type of atom.

   (a) Compound

   (b) Mixture

   (c) Element

   (d) All the above

   (4) Water molecule comprises ...hydrogen atoms and ... oxygen atom.

   (a) One , two

   (b) Three , one

   (c) One , three

   (d) Two , one

   (5) Which of the following is not an example of Physical Properties of substance.?

   (a) Odour

   (b) Melting point

   (c) Density

   (d) Composition

2. The uncertainty in the experimental or the calculated values is indicated by mentioning the number of significant figures. Significant figures are meaningful digits which are known with certainty plus one which is estimated or uncertain. The uncertainty is indicated by writing the certain digits and the last uncertain digit. there are certain rules for determining the Number of significant figures. These are Stated below:

- 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.
- 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.
- Zeros between two non-zero digits are significant. thus, 2.005 has four Significant figures.
- 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.

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.

LAWS OF CHEMICALCOMBINATIONS- The combination of elements to form compounds is governed by the following five basic laws.

1) **Law of Conservation of Mass-** This law was put forth by Antoine Lavoisier in 1789. He performed careful experimental studies for combustion reactions and reached to the conclusion that in all physical and chemical changes, there is no net change in mass during the process. Hence, he reached to the conclusion that matter can neither be created nor destroyed. This is called 'Law of Conservation of Mass'.
2) **Law of Definite Proportions-** This law was given by, a French chemist, Joseph Proust. He stated that a given compound always contains exactly the same proportion of elements by weight.
3) **Law of Multiple Proportions-** This law was proposed by John Dalton. According to this law, 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. For example, hydrogen combines with oxygen to form two compounds, namely, water and hydrogen peroxide.

   Hydrogen + Oxygen→ Water
   2g 16g 18g
   Hydrogen + Oxygen → Hydrogen Peroxide
   2g 32g 34g

   Here, the masses of oxygen (i.e., 16 g and 32 g), which combine with a fixed mass of hydrogen (2g) bear a simple ratio, i.e., 16:32 or 1:2.
4) **Gay Loussac's Law of Gaseous Volumes-** This law was given by Gay Loussac 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 the same temperature and pressure.
5) **Avogadro's Law-** In 1811, Avogadro proposed that equal volumes of all gases at the same temperature and pressure should contain equal number of molecules.

   In 1808, Dalton published 'A New System of Chemical Philosophy', in which he proposed the following:

   (1) Matter consists of indivisible atoms.
   (2) All atoms of a given element have identical properties, including identical mass. Atoms of different elements differ in mass.
   (3) Compounds are formed when atoms of different elements combine in a fixed ratio.
   (4) Chemical reactions involve reorganisation of atoms. These are neither created nor destroyed in a chemical reaction.

1) ………… refers to the closeness of various measurements for the same quantity.
   a) Accuracy
   b) Reliability
   c) Precision
   d) Uncertainty
2) Law of Conservation of mass was put forth by ………. in 1789.
   a) Joseph Proust
   b) Antoine Lavoisier
   c) Joseph Louis
   d) Gay Loussac

3) Which of the following number has two significant figures.

a) 00052

b) 052

c) 52

d) 0.0052

4) ……….. is the agreement of a particular value to the true value of the result.

a) Accuracy

b) Reliability

c) Precision

d) Uncertainty

5) Law of Multiple Proportions proposed by ..

a) Joseph Proust

b) Antoine Lavoisier

c) Joseph Louis

d) John Dalton

Answer Key

MCQ

1. (c) $Fe_2 (So_4)_3$
2. (a) 26.89
3. (b) 21
4. (a) 10
5. (a) 81.398 g
6. (d) I_2
7. (c) 4 g atom of Hydrogen
8. (d) 10^{-21}
9. (a) 24 g of C (12)
10. (c) Constant Composition
11. (c) 4
12. (a) Anion
13. (b) 8.0 g Methane
14. (a) 39.9 g
15. (d) 0.1

Very Short Answer:

1. Chemistry is the branch of science that studies the composition, properties and interaction of matter.
2. Chemical principles are important in diverse areas such as weather patterns, functioning of brain, operation of a computer, chemical industries, manufacturing , fertilizers, alkalis, acids, salts, dyes, polymers, drugs, soaps, detergents, metals, alloys, contribute in a big way to national economy.
3.

Property	Solids	Liquids	Gases
1. Volume	Definite	Definite	Not definite
2. Shape	Fixed	Not fixed, take the shape of container,	Not fixed, takes the shape of the container

4. The components of a mixture can be separated by physical methods like handpicking, filtrations, crystallization, distillation etc.
5.

Pure Substances	Mixtures
Glucose	Air
Gold	Milk
Sodium	

6. Molecules consist of different atoms or same atoms. e.g. molecule of hydrogen contains two atoms of hydrogen whereas molecule of water contain two atoms of hydrogen and one of oxygen.

   Compound is formed when two or more than two different atoms combine in fire propo e.g. water – ration carbon dioxide, sugar etc.
7. The constituents of a compound cannot be separated by physical methods. They can only be separate by chemical methods.
8. Physical properties are those properties which

can be measured or observed without changing the identity or the composition of the substance whereas the measurement of chemical properties require a chemical change to occur e.g. color, odour etc. are physical properties and combustion, basicity etc. are chemical properties.

9. The different system of measurement are English system and the metric system.
10. The SI Unit of density is Kg m^{-3} or kg/m^3

Short Answer:

Ans: 1. A mole is the amount of a substance that contains as many entities (atoms, molecules, or other particles) as there are atoms in exactly 0.012 kg or 12 g of the carbon-12 isotope.

Ans: 2. The molarity of a solution is defined as the number of moles of the solute present per liter of the solution. It is represented by the symbol M. Its value changes with the change in temperature.

Ans: 3. Precision and accuracy: The term precision refers to the closeness of the set of values obtained from identical measurements of a quantity.

Accuracy refers to the closeness of a single measurement to its true value.

Ans: 4. Fundamental units: Fundamental units are those units by which other physical units can be derived. These are mass (M), Length (L), time (T), temperature (°).

Derived units: The units which are obtained by the combination of the fundamental units are called derived units.

Ans: 5. Molality (m) = $\frac{\text{Mole of solute}}{\text{Mass of the solvent in kg}}$

The molality of the solution does not depend upon the temperature.

Ans: 6. Atom: An atom is the smallest particle of an element that takes part in a chemical reaction. It may or may not be capable of independent existence.

Molecule: It is the smallest particle of a substance (element or compound) that is capable of independent existence

Ans: 7. Joule is the SI unit of work or energy

As work $= \text{force} \times \text{distance}$

$= (\text{mass} \times \text{acceleration}) \times \text{distance}$

$= \text{Mass} \times \frac{\text{distance}}{\text{time}^2} \times \text{distance}$

$= \frac{\text{mass} \times (\text{distance})^2}{\text{time}^2}$

Hence $J = \frac{kg \times m^2}{s^2} = kg\ m^2\ s^{-2}$

Long Answer:

Ans: 1. The Law of Multiple Proportions states:

"When two elements combine to form two or more than two chemical compounds than the weights of one of elements which combine with a fixed weight of the other, bear a simple ratio to one another.

Examples:

1. Compound of Carbon and Oxygen: C and O combine to form two compounds CO and CO_2.

In CO_2 12 parts of wt. of C combined with 16 parts by wt. O.

In CO_2 12 parts of wt. of C combined with 32 parts by wt. of O.

If the weight of C is fixed at 12 parts by wt., then the ratio in the weights of oxygen which combine with the fixed wt. of C (= 12) is 16: 32 or 1: 2.

Thus, the weight of oxygen bears a simple ratio of 1: 2 to each other.

2. Compounds of Sulphate (S) and Oxygen (O): S forms two oxides with O, viz., SO_2 and SO_3

In SO_2, 32 parts of wt. of S combine with 32 parts by wt. of O.

In SO_3, 32 parts of wt. of S combine with 48 parts by wt. of O.

If the wt. of S is fixed at 32 parts, then' the ratio in the weights of oxygen which combine with the fixed wt. of S is 32: 48 or 2: 3.

Thus, the weights of oxygen bear a simple ratio of 2: 3 to each other.

Ans: 2. Law of Constant Composition of Definite Proportions states: "A chemical compound is always found, to be made up of the same elements combined together in the same fixed proportion by weight".

Examples:

1. CO_2 may be prepared in the laboratory as follows:

   (i) $CaCO_3 \xrightarrow{Heat} CaO + CO_2\uparrow$

   (ii) $C + O_2 \xrightarrow{Heat} CO_2\uparrow$

   (iii) $CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2\uparrow + H_2O$

   (iv) $2NaHCO_3 \xrightarrow{Heat} Na_2CO_3 + CO_2\uparrow + H_2O$

   In all the above examples, CO2 is made up of the same elements i. e., Carbon (C) and Oxygen (O) combined together in the same fixed proportion by weight of 12: 32 or 3: 8 by weight.

Ans: 3. The empirical formula of a compound expresses the simplest whole-number ratio of the atoms of the various elements present in one molecule of the compound.

For example, the empirical formula of benzene is CH and that of glucose is CH2O. This suggests that in the molecule of benzene one atom of Carbon (C) is present for every atom of Hydrogen (H). Similarly in the molecule of glucose (CH2O), for every one atom of C, there are two atoms of H and one atom of O present in its molecule. Thus, the empirical formula of a compound represents only the atomic ratio of various elements present in its molecule.

The molecular formula of a compound represents the true formula of its molecule. It expresses the actual number of atoms of various elements present in one molecule of a compound. For example, the molecular formula of benzene is C_6H_6 and that of glucose is $C_6H_{12}O_6$. This suggests that in one molecule of benzene, six atoms of C and 6 atoms of H are present. Similarly, one molecule of glucose ($C_6H_{12}O_6$) actually contains 6 atoms of C, 12 atoms of H, and 6 atoms of O.

Relation between the empirical and molecular formula

Molecular formula = n × Empirical formula where n is an integer such as 1, 2, 3...

When n = 1; Molecular formula = Empirical formula

When n = 2; Molecular formula = 2 × Empirical formula.

The value of n can be obtained from the relation.

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

The molecular mass of a volatile substance can be determined by Victor Meyer's method or by employing the relation.

Molecular mass = 2 × vapour density.

Empirical formula mass can however be obtained from its empirical formula simply by adding the atomic masses of the various atoms present in it.

Thus, the empirical formula mass of glucose CH_2O

= 1 × 12 + 2 × 1 + 1 × 16 = 30.0 u.

Ans: 4. 2 mols of HNO_3 are produced by 3 mols of NO_2

7.33 mol HNO_3 are produced by $\frac{3 \times 7.33}{2}$ mol of NO_2

= 10.995 mols.

Ans: 5. Molar mass of $NaNO_3$ = 23 + 14 + 3 × 16 = 85 g mol^{-1}

Molarity = Number of moles of solute Volume of solution in L

$= \frac{0.83 \times 1000}{85 \times 50}$

= 0.196 M.

Assertion Reason Answer:

1. (i) Both A and R are true and R is the correct explanation of A.
2. (ii) Both A and R are true but R is not the correct explanation of A.

Case Study Answer:

1. **Answer:**

   (1) (b) Liquid

   (2) (c) Solid

   (3) (c) Element

   (4) (d) Two , one.

   (5) (d) Composition

2. **Answer:**

   (1) (c) Precision

   (2) (b) Antoine Lavoisier

   (3) (d) 0.0052

   (4) (a) Accuracy

   (5) (d) John Dalton

◆ ◆

Structure of Atom

2

Introduction

The word "atom" has been derived from the Greek word 'atoms' which mans '**indivisible**'. These early ideas were mere speculation and there was no way to test them experimentally.

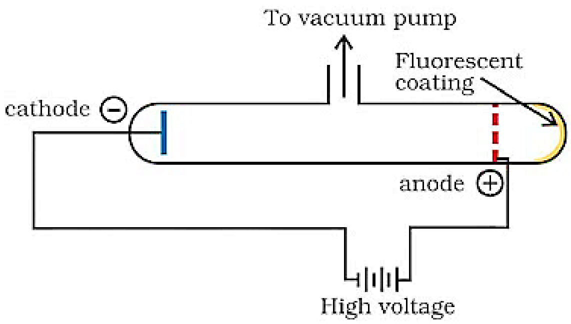
Atomic Structure:

Atom is made up of smaller units like proton, neutron and electron. Some other particles like positron, neutrino, antineutrino, π-meson, μ-meson, k meson etc. are also present which are very short lived.

Particle	Mass	Charge	Special Remark
Electron	9.1×10^{-31} kg	-1.6×10^{-19} C	Discovered by J.J. Thomson
Proton	1.67×10^{-27} kg	$+1.6 \times 10^{-19}$ C	Discovered by Gold Stein
Neutron	1.67×10^{-27} kg		Discovered by Chadwick
Positron		$+1.6 \times 10^{-19}$	Anderson
π meson	π° – 268 Me $\pi+$ – 273 Me π – 273 Me		Yukawa

Discovery of Electron

In 1879, **William Crooks** studied the conduction of electricity through gases at low pressure. He performed the experiment in a discharge tube which is a cylindrical hard glass tube about 60 cm in length. It is sealed at both the ends and fitted with two metal electrodes. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages.



J.J. Thomson took a discharge tube and applied a voltage of a 10000-volt potential difference across it at a pressure of 10–2 mm of Hg. He found some glowing behind anode. It means some invisible rays produced at cathode strike behind anode and produce fluorescence. He named them cathode rays.

Properties of Cathode Rays

i. These rays have mechanical energy and travel in straight line.

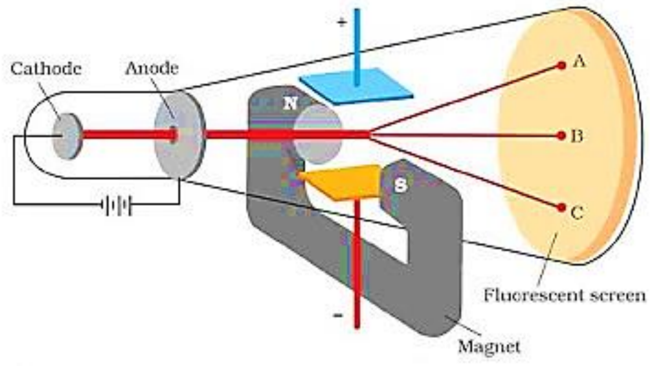
ii. These rays are deflected towards positive plate of electric field. It means these are made up of negatively charged particle called **electron**.

iii. Colour observed is independent from nature of gas.

iv. Mulliken determined the charge on electron which is 1.602×10^{-19}C.

v. Specific charge on electron is calculated by J.J. Thomson.

Charge to mass ratio



J.J. Thomson for the first time experimentally determined charge/mass ratio called e/m ratio for the electrons. For this, he subjected the beam of electrons released in the discharge tube as cathode rays to influence the electric and magnetic fields. These were acting perpendicular to one another as well as to the path followed by **electrons**.

According to Thomson, the amount of deviation of the particles from their path in presence of electrical and magnetic field depends on,

1. Magnitude of the negative charge on particle
2. Mass of particle
3. Strength of magnetic field

When electric field is applied, deviation from path takes place. If only electric field is applied, cathode rays strike at A. If only magnetic field is applied, cathode rays strike at C. In absence of any field, cathode rays strike at B.

By carrying out accurate measurements on the amount of deflections observed by the electrons on the electric field strength or magnetic field strength, Thomson was able to determine the value of $e/m_e = 1.758820 \times 10^{11}$ C kg^{-1}

where me = Mass of the electron in kg

e = magnitude of charge on the electron in coulomb (C).

Discovery of anode rays

In 1886, Goldstein modified the discharge tube by using a perforated cathode. On reducing the pressure, he observed a new type of luminous rays passing through the holes or perforations of the cathode and moving in a direction opposite to the cathode rays. These rays were named as positive rays or anode rays or as canal rays. Anode rays are not emitted from the anode but from a space between anode and cathode.

Properties of anode rays

1. These rays deflect towards negative plate of applied electric field. It means these are made up of positively charged particle.
2. Property of anode rays depends on nature of gas.
3. These rays travel in straight line and have mechanical energy.

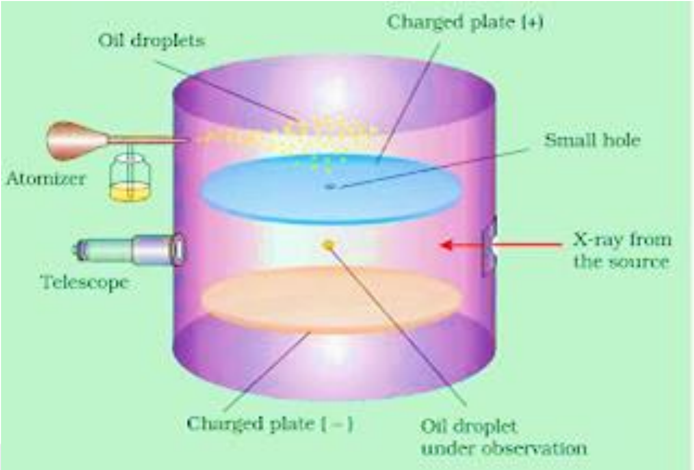
Discovery of Neutron

Chadwick in 1932 found the evidence for the production of neutron in given reaction.

$$_4Be^9 + {}_2He^4 \longrightarrow {}_6C^{12} + {}_0n^1$$

Neutron is chargeless particle and have mass equal to proton.

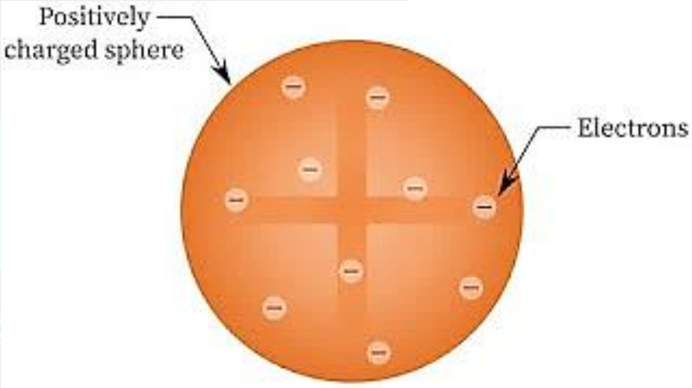
Millikan’s Oil Drop Experiment



In this experiment, some fine oil droplets were allowed to enter through a tiny hole into the upper plate of electrical condenser. These oil droplets were produced by atomizer. The air in the chamber was subjected to the ionization by X-rays. The electrons produced by the ionization of air attach themselves to the oil drops.

Thus, oil droplets acquire negative charge. When sufficient amount of electric field is applied, the motion of the droplets can be accelerated, retarded or made stationary. Millikan observed that the smallest charge found on them was −1.6 × 10–19 coulomb and the magnitude of electrical charge, q on the droplets is always an integral multiple of the electrical charge ‘e’ i.e., q = ne

Thomson’s Model of Atom

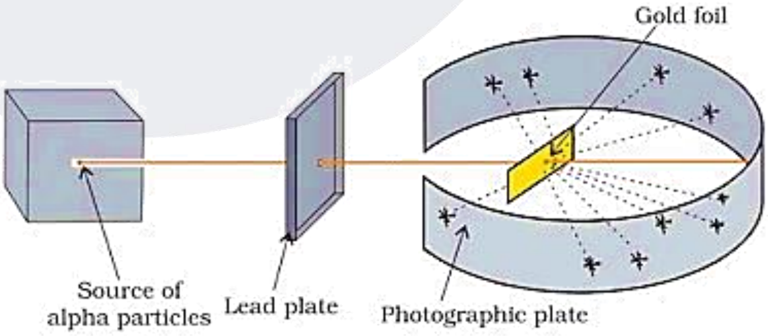


J.J. Thomson in 1898, proposed a model of atom which looked more or less like plum pudding or raisin pudding. He assumed atom to be a spherical body in which electrons are unevenly distributed in a sphere having positive charge which balance the electron’s charge. It is called Plum pudding model.

Important Feature of This Model: The mass of the atom is assumed to be uniformly distributed over whole atom.

Failure: This model was able to explain the overall neutrality of the atom, it could not satisfactorily, explain the results of scattering experiments carried out by Rutherford in 1911.

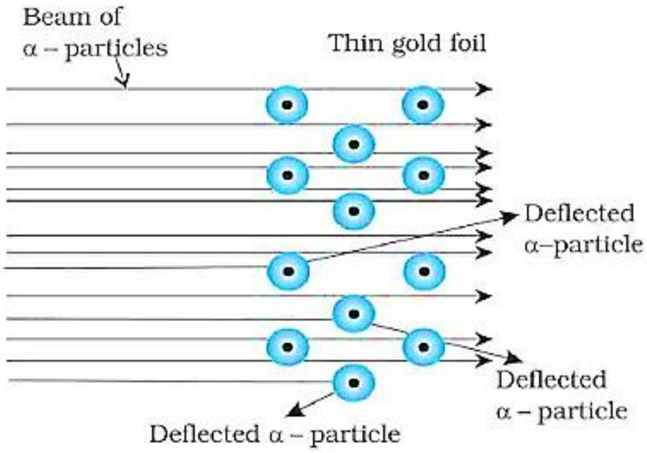
Rutherford's Model



Rutherford in 1911, performed some scattering experiments in which he bombarded thin foils of metals like gold, silver, platinum or copper with a beam of fast moving a-particles. The thin gold foil had a circular fluorescent zinc sulphide screen around it. Whenever a-particles struck the screen, a tiny flash of light was produced at that point.

From these experiments, he made the following observations:

1. Most of the α-particles pass without any deviation.
2. Few particles deviate with small angle.
3. Rare particles retrace its path or show deflection greater than 90°.



On the basis of these observation, he proposed a model.

1. Atom is of spherical shape having size of order 10–10 meters.
2. Whole mass is concentrated in centre called nucleus having size of order 10–15 meters.
3. Electron revolves around the nucleus in circular path like planets revolve around sun.

Limitation: This model could not explain stability of atom. According to Maxwell's classic theory, an accelerated charged particle liberates energy. So, during revolution, it must radiate energy and by following the spiral path it should comes on nucleus.

Atomic number

It is equal to the number of protons present in the nucleus of an atom. Atomic number is designated by the letter 'Z'. In case of neutral atom atomic number is equal to the number of protons and even equal to the number of electrons in atom.

Z = Number of protons (p) = Number of electrons (e)

Mass number

It is equal to the sum of the positively charged protons (p) and electrically neutral neutrons (n). Mass number of an atom is designated by the letter 'A'.

Mass number (A) = Number of protons (p or Z) + Number of neutrons (n)

Note: The atom of an element X having mass number (A) and atomic number (Z) may be represented by a symbol $_ZX^A$.

Isotopes

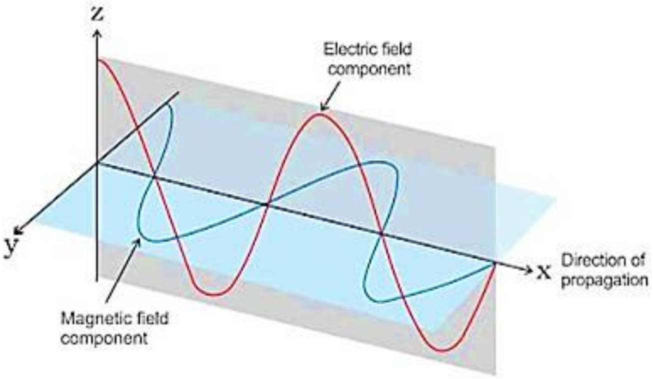
Atoms with identical atomic number but different atomic mass number are known as Isotopes. Isotopes of Hydrogen $_1H^1$, $_1H^2$ and $_1H^3$

Isobars

Isobars are the atom with the same mass number but different atomic number, for example $_6C^{14}$ and $_7N^{14}$

Electromagnetic Waves Theory

This theory was put forward by James Clark Maxwell in 1864. Electromagnetic Waves are the waves which are produced by varying electric field and magnetic field which are perpendicular to each other in the direction perpendicular to both of them.



The main points of this theory are as follows:

1. The energy is emitted from any source continuously in the form of radiations and is called the radiant energy.
2. The radiations consist of electric and magnetic fields oscillating perpendicular to each other and both perpendicular to the direction of propagation of the radiation.
3. The radiations possess wave character and travel with the velocity of light 3×10^8 m/sec.
4. These waves do not require any material medium for propagation. For example, rays from the sun reach us through space which is a non-material medium.

Characteristics of a Wave

Wavelength (λ): It is the distance between two consecutive crests or troughs and is denoted by λ.

Frequency (v): It is the number of waves passing through a given point in one second. The unit frequency is hertz or cycle per second.

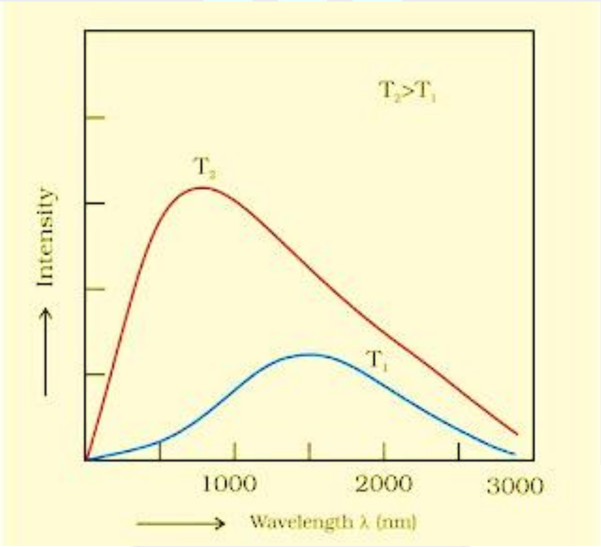
Wave number: It is the number of waves in a unit cycle. wave number =1λ=1λ

Velocity: Velocity of a wave is defined as the linear distance travelled by the wave in one second. It is represented by c and is expressed in m/sec.

Amplitude: Amplitude of a wave is the height of the crest or the depth of the through. It is represented by V and is expressed in the units of length.

Black Body Radiations

Black-body is an ideal body which emits and absorbs radiations of all frequencies. The radiation emitted by these bodies is called **black-body radiation**.



At a given temperature, the intensity and frequency of the emitted radiation depends is temperature. At a given temperature, the intensity of radiation emitted increases with decrease of wavelength.

Photoelectric Effect

When light of a suitable frequency is allowed to incident on a metal, ejection of electrons take place. This phenomenon is known as photo electric effect.

Observations in Photoelectric Effect

1. Only photons of light of certain minimum frequency called threshold frequency (v_0) can cause the photoelectric effect. The value of v_0 is different for different metals.
2. The kinetic energy of the electrons which are emitted is directly proportional to the frequency of the striking photons and is quite independent of their intensity.
3. The number of electrons that are ejected per second from the metal surface depends upon the intensity of the striking photons or radiations and not upon their frequency.

Explanation of Photoelectric Effect

Einstein in (1905) was able to give an explanation of the different points of the photoelectric effect using Planck's quantum theory as under:

1. Photoelectrons are ejected only when the incident light has a certain minimum frequency (threshold frequency ν_0).
2. If the frequency of the incident light (ν) is more than the threshold frequency (ν_0), the excess energy ($h\nu - h\nu_0$) is imparted to the electron as kinetic energy.
3. On increasing the intensity of light, more electrons are ejected but the energies of the electrons are not altered.

   K.E. of the ejected electron.

$$\frac{1}{2}mv^2 = h\nu - h\nu_0$$

Planck's Theory

According to this theory, energy cannot be absorbed or released continuously but it is emitted or released in the form of small packets called quanta. In case of light this quantum is known as photon. This photon travels with speed of light. Energy of the photon is directly proportional to frequency.

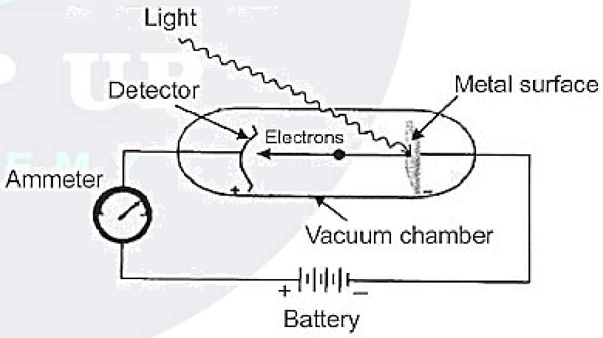
$$E \propto \nu$$

$$E = h\nu$$

h is ***Planck's constant***, value is 6.62×10^{-34} Js

Bohr's Model

1. Niels Bohr in 1913, proposed a new model of atom on the basis of Planck's Quantum Theory. The main points of this model are as follows:
2. Atom is of spherical shape having size (of order 10^{-10} metre).
3. Whole mass is concentrated in centre called nucleus (having order of size 10^{-15} metre).
4. Electron revolves around nucleus only in limited circular path and he assumed that electron does not radiate energy during its revolution in permitted paths.
5. Only those orbits are allowed whose orbit angular momentum is integral multiple of h2πh2π.
6. $mvr = nh/2\pi$, where n = 1, 2, 3, 4...
7. When electron absorbs energy, it jumps to higher orbit and when it comes back, it radiates energy. This postulate explain spectra.



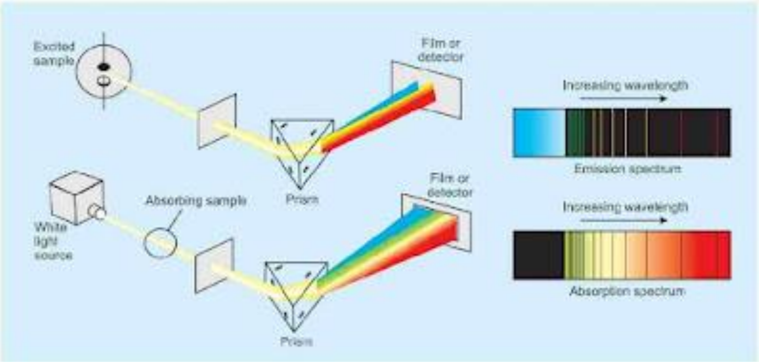
Achievements of Bohr's Theory

1. Bohr's theory has explained the stability of an atom.
2. Bohr's theory has helped in calculating the energy of electron in hydrogen atom and one electron species.
3. Bohr's theory has explained the atomic spectrum of hydrogen atom.

Limitations of Bohr's Model

1. The theory could not explain the atomic spectra of the atoms containing more than one electron or multielectron atoms.
2. Bohr's theory failed to explain the fine structure of the spectral lines.
3. Bohr's theory could not offer any satisfactory explanation of Zeeman effect and Stark effect.
4. Bohr's theory failed to explain the ability of atoms to form molecule formed by chemical bonds.
5. It was not in accordance with the Heisenberg's uncertainty principle.

Spectra



The most compelling evidence for the quantization of energy comes from spectroscopy. Spectrum word is taken from Latin word which means appearance. The record of the intensity transmitted or scattered by a molecule as a function of frequency or wavelength is called its spectrum.

Cosmic rays < gamma rays < x rays < ultraviolet rays < visible rays < infra red < micro waves < radio waves.

Line Spectrum of Hydrogen Atom

When electric discharge is passed through hydrogen gas enclosed in discharge tube under low pressure and the emitted light is analysed by a spectroscope, the spectrum consists of a large number of lines which are grouped into different series. The complete spectrum is known as hydrogen spectrum.

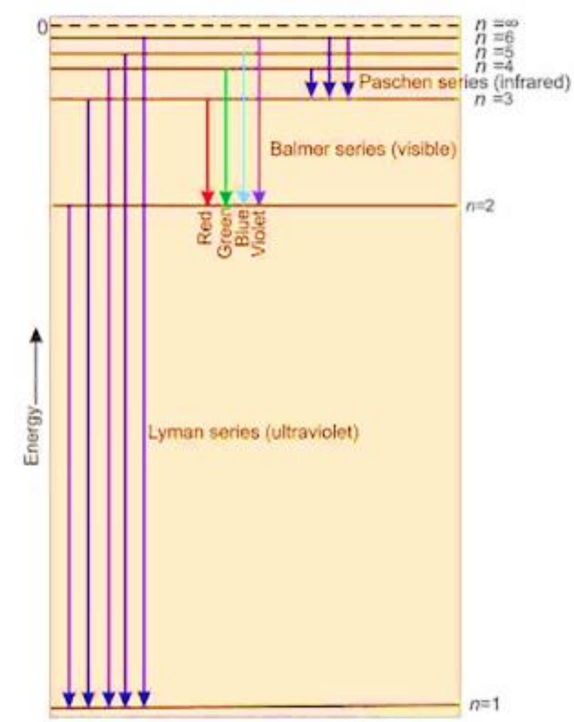
On the basis of experimental observations, Johannes Rydberg noted that all series of lines in the hydrogen spectrum could be described by the following expression:

wave number = 1λ = R(1n21 − 1n22)1λ = R(1n12 - 1n22)

R = Rydberg constant

R = 109678 cm^{-1}

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



Zeeman Effect

When spectral line (source) is placed in magnetic field, spectral lines split up into sublines. This is known as zeeman effect.

Stark Effect

If splitting of spectral lines take place in electric field, then it is known as stark effect.

Dual Behaviour of Matter (de Broglie Equation)

De Broglie in 1924, proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle like and wave like properties. This means that like photons, electrons also have momentum as well as wavelength.

Assume light have wave nature, then its energy should be given by Planck's theory

$$E = h\nu E = h\nu \qquad \text{...(i)}$$

If it has particle nature, then its energy should be given by Einstein relation,

$$E = mc^2 \qquad \text{...(ii)}$$

On comparing equation (i) and (ii),

$$h\nu = mc^2$$

$$\lambda = hmc \text{ (for light)} \qquad \text{...(iii)}$$

For other matter,

$$\lambda = hmv \qquad \text{...(iv)}$$

$$\lambda = hp \qquad \text{...(v)}$$

where p = momentum

This equation is called de Broglie equation.

Heisenberg's Uncertainty Principle

It states that, "It is impossible to measure simultaneously the exact position and exact momentum of a microscopic particle".

If uncertainty in position = Δ × and

Uncertainty in momentum = ΔP

When both are measured simultaneously, according to this principle,

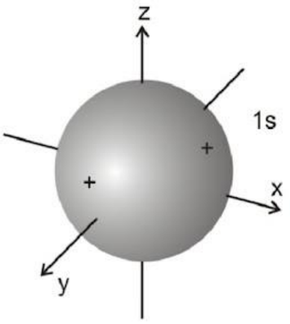
$$\Delta \times \Delta P \geq h4\pi$$

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.

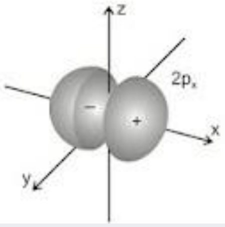
1. **Principal quantum number (n)**: It identifies shell, determines sizes and energy of orbitals. It is indicated by 'n' and its values are 1, 2, 3, 4...
2. **Azimuthal quantum number (l)**: Azimuthal quantum number. 'l' is also known as orbital angular momentum or subsidiary quantum number. l. It identifies 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., The number of orbitals in a sub shell = 2l + 1. For a given value of n, it can have n values ranging from 0 to n-1.
3. **Magnetic 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, ml = – l, – (l–1), – (l–2)... 0,1...(l–2), (l–1), l
4. **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.

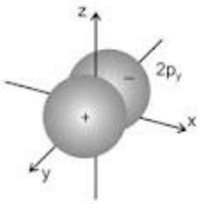
Shape of Atomic Orbitals

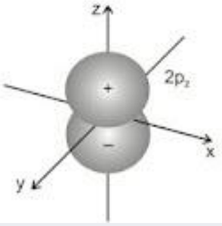


Shapes of s-orbitals: s-orbital is present in the s-sub shell. For this sub shell, l = 0 and ml = 0. Thus, s-orbital with only one orientation has a spherical shape with uniform electron density along all the three axes. The probability of Is electron is found to be maximum near the nucleus and decreases with the increase in the distance from the nucleus.

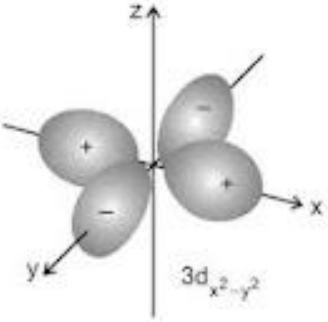
Shapes of p-orbitals: p-orbitals are present in the p-subshell for which l = 1 and ml can have three possible orientations −1, 0, +1. Thus, there are three orbitals in the p-subshell which are designated as px, py and pz orbitals depending upon the axis along which they are directed. The general shape of a p-orbital is dumb-bell consisting of two portions known as lobes.

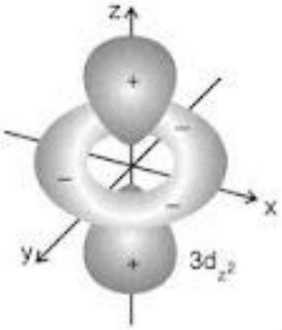


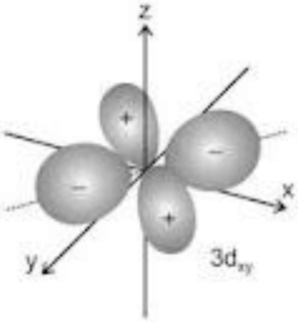


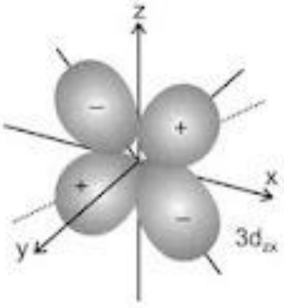


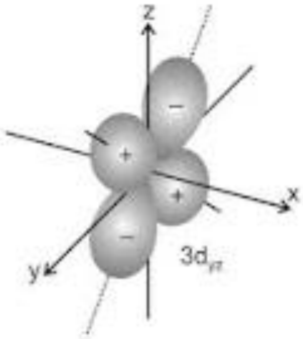
Shapes of d-orbitals: d-orbitals are present in d-subshell for which l = 2 and ml = -2, -1, 0, +1 and +2. This means that there are five orientations leading to five different orbitals. d orbitals are of five types: d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2}









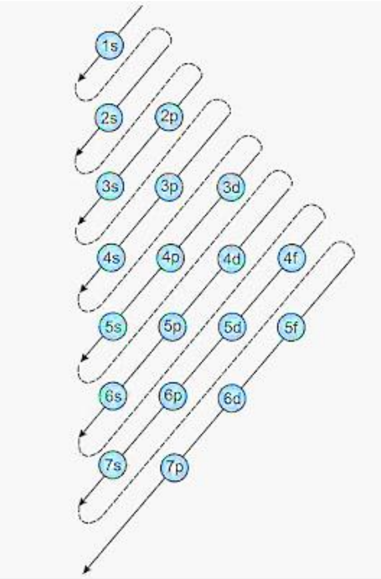


Electronic Configuration

Distribution of electron in various orbitals is known as electronic configuration. The electrons filled in orbitals must obey the following rules-

- Aufbau’s principle
- Pauli’s exclusion principle
- Hund’s rule of maximum multiplicity

1. **Aufbau’s principle:** According to this principle, orbitals with lowest energy are filled before the orbitals having higher energy.

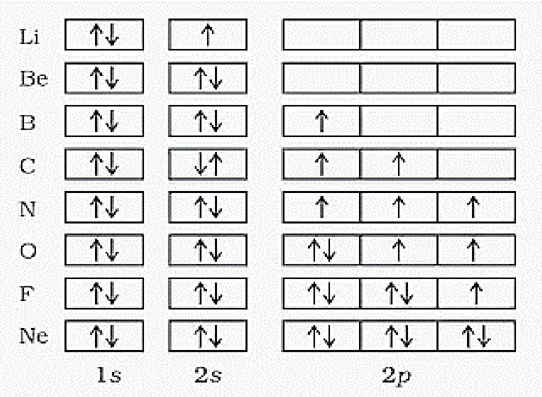


1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p

(n + l) rule (Bohr Bury's Rule)

According to this, the orbital which has lower value of (n + l) is lower in energy.

2. **Pauli's exclusion principle:** According to this principle, in an atom, no two electrons have same value of all the four quantum numbers. In the same orbital, electron always accommodate in opposite spins. An orbital can have a maximum of two electrons, with opposite spin.
3. **Hund's rule of maximum multiplicity:** According to this rule, electrons are distributed among the orbital of a subshell in such a way so as to give the maximum number of unpaired electrons with a parallel spin.



Li	↑↓	↑			
Be	↑↓	↑↓			
B	↑↓	↑↓	↑		
C	↑↓	↓↑	↑	↑	
N	↑↓	↑↓	↑	↑	↑
O	↑↓	↑↓	↑↓	↑	↑
F	↑↓	↑↓	↑↓	↑↓	↑
Ne	↑↓	↑↓	↑↓	↑↓	↑↓
	1s	2s		2p	

Discovery of Proton

Last Updated on July 6, 2022 By Mrs. Shilpi Nagpal 3 Comments

Since the atom as a whole is electrically neutral and the presence of negatively charged particles in it was established, therefore, it was thought that some positively charged particles must also be present in the atom.

Goldstein in 1886 performed discharge tube experiment in which he took perforated cathode and a gas at low pressure was kept inside the tube, as before.

1)On passing high voltage between the electrodes, it was found that some rays were coming from the side of the anode which passed through the holes in the cathode and produced green fluorescence on the opposite glass wall coated with zinc sulphide. These rays were called anode rays or canal rays or positive rays.

Properties of anode rays

1) They travel in straight line.

2) They are made up of material particles.

3) They are positively charged.
4) The value of e/m depend upon the nature of gas taken inside the discharge tube.
5) The value of the charge on the particles constituent the anode rays is also found to depend upon the nature of the gas taken inside the discharge tube.
6) The mass of the particle constituting the anode rays is also found to be different for different gases taken in discharge tube.

The charge on these particles is found to be same as that on the electron i.e. 1.6 × 10-19 coulombs per gram.

The ratio, charge/mass, for each of the particle is found to be 9.58 × 10-24 g.

These particles were termed as protons.

A proton may be defined as that fundamental particle which carries 1 unit positive charge and has a mass nearly equal to that of hydrogen atom.

Discovery of neutron

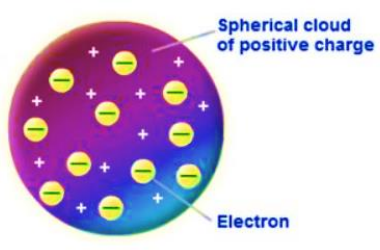
Chadwick in 1932, performed some scattering experiment in which he bombarded some light elements like beryllium and boron with fast moving Alpha particles. He found that some new particles were emitted which carried no charge ie. were neutral but had a mass nearly equal to that of proton. This particle was termed neutrons.

A neutron may be defined as those fundamental particles which carries no charge but has a mass nearly equal to that of hydrogen atom or proton.

Rutherford's Model of an Atom

Thomson's model of atom

J.J. Thomson in 1904, proposed that an atom was a sphere of positive electricity in which were embedded number of electrons. The stability of the atom was explained as a result of the balance between the repulsive forces between the electrons and their attraction towards the centre of the positive Sphere. This model is compared with a watermelon in which seeds are embedded or with a cake or pudding in which raisins are embedded. That is why this model is called as raisin pudding model a watermelon model.

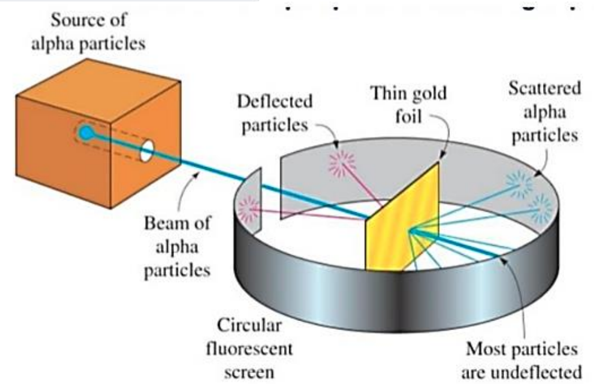


Limitation

This model could not explain the stability of the atom.

Rutherford Model of atom

Rutherford in 1911, performed scattering experiment in which he bombarded thin walls of metals like gold, silver, Platinum or copper with a beam of fast-moving Alpha particles. The source of Alpha particles was radium, a radioactive substance, placed in a block of lead. Slits were used to get a fine beam. The presence of Alpha particles at any point around the thin foil of gold after striking it was detected with the help of a circular zinc sulphide. The point at which an Alpha particle strikes this screen, a flash of light is given out.

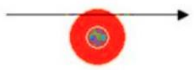


Observation

1) Most of the Alpha particles passed through the foil without undergoing any deflection.
2) Few Alpha particles underwent deflection through small angles.
3) Very few were deflected back through an angle greater than 90°

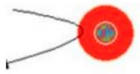
Conclusion

1) Since most of the Alpha particles passed through the foil without undergoing any deflection, there must be sufficient empty space within the atom.



2) Since few alpha particles were deflected through small angles and alpha particles were positively charged particles, these could be deflected only by some positive body present within the atom. The alpha particles deflected were those which passed very close to this positive body.

3) Since some alpha particles were deflected back and alpha particles are heavy particle, these could be deflected back only when they strike some heavier body inside the atom.



4) Since the number of alpha particles deflected back is very very small, this shows that the heavy body present in an atom must be occupying a very very small volume.

The small heavy positively charged body present within the atom was called nucleus.

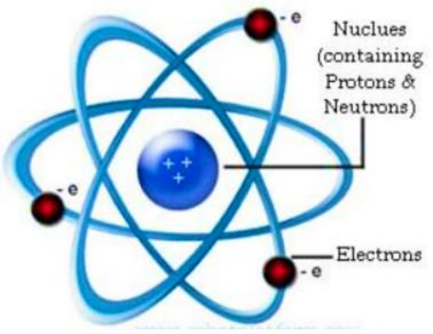
Rutherford Model of an atom

(1) Nucleus is very small in size, carries positive charge and in which the entire mass of the atom is concentrated.

(2) Since electrons have negligible mass, the mass of the atom is mainly due to protons and neutrons.

(3) Protons and neutrons must be present in the nucleus.

(4) Extranuclear part is the space around the nucleus in which the electrons were distributed.



Drawback of Rutherford's Model of an atom

(1) Inability to explain the stability of atom

An atom consists of a small, heavy positively charged nucleus in the centre and the electrons were revolving around it. This model was compared with the solar system in which the planets were revolving around the sun and continue to move in their fixed circular paths because the force of attraction was balanced by the centrifugal force.

According to Maxwell's electromagnetic theory, whenever a charged particle like electron is revolving in a field of force like that of the nucleus, it loses energy continuously in the form of electromagnetic radiation. This is because when a particle is revolving, it undergoes acceleration due to change in direction even if the speed remains constant. Thus, the orbit of the revolving electron will keep on becoming smaller and smaller, following a spiral path and ultimately the electron should fall into the nucleus. The atom should collapse.

(1) Rutherford model could not explain the stability of the atom.

(2) Inability to explain the line spectra of the elements.

(3) Inability to describe distribution of electrons and energies of electrons.

Electromagnetic Wave Theory

Electromagnetic wave theory

This theory was put forward by James clark Maxwell in 1864.

The main points of this theory are:

1) The energy is emitted from any source continuously in the form of radiations and is called the radiant energy.

2) The radiations consist of electric and magnetic fields oscillating perpendicular to each other and both perpendicular to the direction of propagation of the radiation.

3) The radiations possess wave character and travel with the velocity of light.

The radiations are called electromagnetic radiations or electromagnetic waves.

4) These waves do not require any material medium for propagation.

Characteristics of a wave

1) Wavelength

Wavelength of a wave is defined as the distance between any two consecutive crest or trough.

It is represented by λ (Lambda) and is expressed in A° or m or cm or nm or pm.

1 A° = 10^{-8} cm = 10^{-10} m

1nm = 10^{-9} m, 1pm= 10^{-12} m

2) Frequency

Frequency of a wave is defined as the number of waves passing through a point in 1 seconds.

It is represented by ν (nu) and is expressed in hertz(Hz) or cycles/second or sec-1

3) Velocity

Velocity of a wave is defined as the linear distance travelled by the wave in 1 seconds.

It is represented by c and is expressed in cm/sec or m/sec.

4) Amplitude

Amplitude of a wave is the height of the crest or the depth of the trough.

It is represented by a and is expressed in the units of length.

5) Wavenumber

Wavenumber is defined as the number of waves present in 1 cm length.

It will be equal to the reciprocal of the wavelength.

It is represented by $\bar{v}$

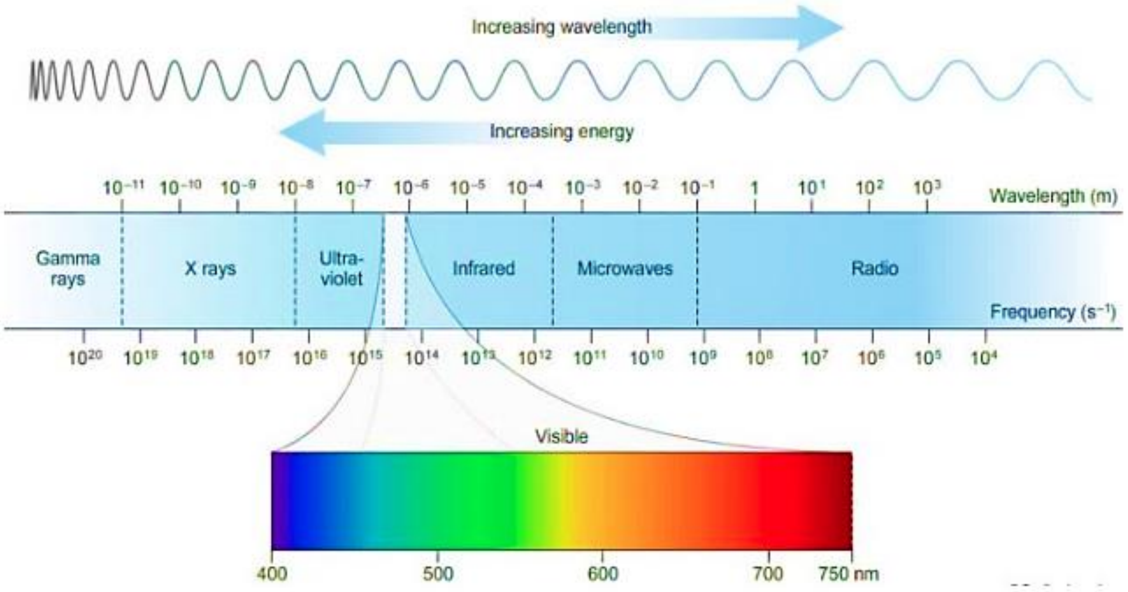
Relation between velocity, wavelength and frequency of a wave

$$C = \lambda v$$

Electromagnetic Spectrum

The different types of electromagnetic radiations differ only in their wavelength and hence frequency.

Their Wave length increases in the following order:



Electromagnetic spectrum

When these electromagnetic radiations are arranged in order of their increasing wavelength or decreasing frequencies, the complete spectrum obtained is called electromagnetic spectrum.

Limitations of electromagnetic wave theory

It could not explain the:

1) The phenomena of black body radiation
2) The photoelectric effect
3) The variation of heat capacity of solid as a function of temperature.
4) The line spectra of atoms with special reference to hydrogen.

Black body radiation

If any substance with high melting point is heated, it first becomes red, then yellow and finally begins to glow with white and then blue light.

If the substance being heated is a black body (which is a perfect absorber and perfect radiator of energy i.e. which can emit and absorb all frequencies) the radiations emitted is called black body radiation

The energy of any electromagnetic radiation is proportional to its intensity, i.e. square of amplitude and is independent of its frequency or wavelength.

The change of colours shows that on heating, the frequency of the radiations emitted is increasing.

Intensity versus wavelength

At a given temperature, intensity of radiation emitted increases with decrease of wavelength, reaches a maximum value at a particular wavelength and then start decreasing with further decrease of wavelength.

Photoelectric effect

When radiations with certain minimum frequency (νo) strike the surface of a metal, the electrons are ejected from the surface of the metal. This phenomenon is called Photoelectric effect

The electrons emitted are called photoelectrons.

1) The electrons are ejected only if the radiation striking the surface of the metal has at least a minimum frequency(νo). If the frequency is less than νo, no electrons are ejected(hνo). This value is called threshold frequency.

   The minimum energy required to eject the electrons is called work function (Wo)
2) The velocity of the electron ejected depends upon the frequency of the incident radiation and is independent of its intensity.
3) The number of photoelectrons ejected is proportional to the intensity of incident radiation.

Planck's Quantum Theory

Max Planck in 1900, put forward a theory known after his name as Planck's Quantum theory

The main points of this theory are:

1) The radiant energy is emitted or absorbed not continuously but discontinuously in the form of small discrete packets of energy. Each such packet of energy is called quantum. In case of light ,the quantum of energy is called Photon.
2) The energy of each quantum is directly proportional to the frequency of the radiation ie.

   $$E=h\nu$$

   Where h is the proportionality constant, called Planck's Constant.

   Its value is 6.626×10^{-27} erg sec or 6.626×10^{-34} joule sec.
3) The total amount of energy emitted or absorbed by a body will be some whole number quanta.

   $$\text{Hence } E= nh\nu$$

Explanation of black body radiation

When some solid substance is heated, the atoms of the substance are set into oscillations and emit radiations of frequency, ν. Now, as heating is continued, more and more energy is being absorbed by the atoms and they emit radiations of higher and higher frequency. As red light has minimum frequency and yellow light has higher frequency, therefore the body on heating becomes first red, then yellow and so on.

Explanation of Photoelectric Effect

1) When light of some particular frequency falls on the surface of metal, the photon gives its entire energy to the electron of the metal atom. The electron will be detached from the metal atom only if the energy of the photon is sufficient to overcome the force of attraction of the electron by the nucleus. That is why photoelectrons are ejected only when the incident light has a certain minimum frequency (threshold frequency ν0)
2) If the frequency of the incident light is more than the threshold frequency ,the excess energy is imparted to the electron as kinetic energy.

   Greater is the frequency of the incident light, greater is the kinetic energy of emitted electron.
3) When the intensity of light is increased, more electrons are ejected but the energies of these electrons are not altered.

Absorption and Emission Spectra

Electromagnetic spectrum

The electromagnetic spectrum consists of radiation of different wavelength and frequency.

An instrument used to separate the radiations of different wavelength is called spectroscope or spectrograph.

A spectroscope consists of a prism or a diffraction grating for the dispersion of radiation and a photographic film to examine the emergent radiation with the human eye.

The branch of science dealing with the study of spectra is called spectroscopy.

The spectra are broadly classified into:

1) Emission spectra
2) Absorption Spectra

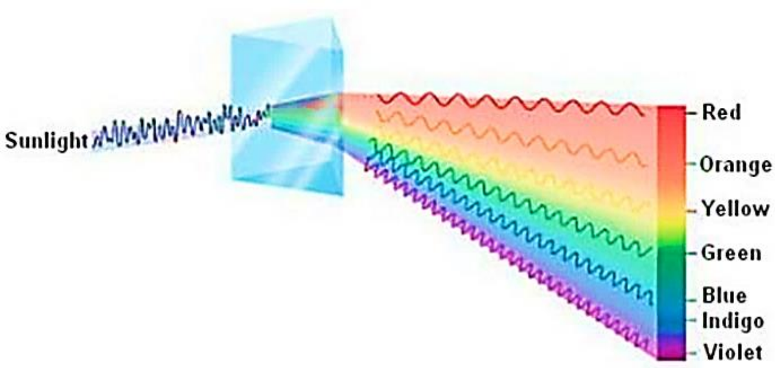
Emission spectra

When the radiations emitted from some source eg: from the sun or by-passing electric discharge through a gas at low pressure or by heating some substance to high temperature is passed directly through the prism and then received on the photographic plate, the spectrum obtained is called emission spectrum.

Depending upon the source of radiation, the emission spectra are mainly of two types:

1) Continuous spectrum

When white light from any source is analysed by passing through a prism, it is observed that it splits up into 7 different wide bands of colour. These colours are so continuous that each of them merges into the next. Hence the spectrum is called continuous spectrum.



On passing through the prism, red colour with the longest wavelength is deviated least while violet colour with shortest wavelength is deviated the most.

2) Line Spectra

When some volatile salt is placed in the bunsen flame or an electric discharge is passed through a gas at low pressure, light is emitted. The colour of light emitted depends upon the nature of substance.

Sodium emits yellow light while potassium gives out violet light.

If this light is resolved in a spectroscope, some isolated coloured lines are obtained on the photographic plates separated from each other by dark spaces. This spectrum is called line emission spectrum on line spectrum.

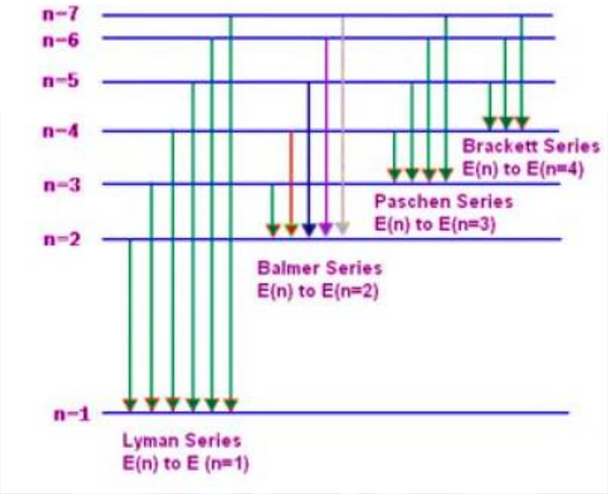
Each line in the spectrum corresponds to a particular wavelength. Sodium always gives two yellow lines.

Absorption spectra

White light from any source is passed through the solution or vapours of a chemical substance and then analysed by the spectroscope, it is observed that some dark lines are obtained. These dark lines are supposed to result from the fact that when the white light is passed through the chemical substance,, the radiations of certain wavelengths are absorbed, depending upon the nature of the element.

The dark lines are at the same place where coloured lines are obtained in the emission spectra for the same substance. The wavelength absorbed were same as were emitted in the emission spectra. The spectrum thus obtained is called absorption spectrum.

Emission spectrum of Hydrogen



When hydrogen gas at low pressure is taken in the discharge tube and the light emitted on passing electric discharge is examined with a spectroscope, the spectrum obtained is called the emission spectrum of hydrogen. It is found to consist of a large number of lines which are grouped into different series ,named after the discoverer.

Rydberg in 1890 gave a very simple theoretical equation for the calculation of wavelength of these lines.

Where R is a constant ,called Rydberg constant and has a value of 109677 cm^{-1} or 1.097 × 107 m^{-1}

n1 and n2 are whole numbers and for a particular series, n1 is constant and n2 varies.

Rydberg's constant for hydrogen

Where Z is the atomic number.

Summary-

1. **Atomic number**: It is equal to the number of protons in the nucleus of an atom.
2. **Mass number**: It is equal to the sum of the positively charged protons (p) and electrically neutral neutrons (n).
3. **Isotopes**: Isotopes are the atoms of the same element which have the same atomic number but different mass numbers.
4. **Isobars:** Isobars are the atoms of different elements having the same mass number but different atomic numbers.
5. **Isoelectronic species**: These are those species which have same number of electrons.
6. **Radiations**: These are defined as the emission or transmission of energy through space in the form of waves.
7. **Electromagnetic waves**: The waves which consist of oscillating electric and magnetic fields are called electromagnetic waves.

8. **Electromagnetic radiations**: Those radiations which are associated with electric and magnetic field are called electromagnetic radiations.
9. **Electromagnetic spectrum**: The arrangement of the various types of electromagnetic radiations in the order of increasing or decreasing wavelengths or frequencies is known as electromagnetic spectrum.
10. **Wavelength (λ)**: It is the distance between successive points of equal phase of a wave.
11. **Frequency (f)**: The number of waves that pass a given point in one second is known as the frequency.
12. **Time period (T)**: Time taken by the wave for one complete cycle or vibration is called time period.
13. **Velocity (v)**: It is the distance travelled by a wave in one second.
14. **Wave number**: It is defined as the number of wavelengths per unit length.
15. **Threshold frequency**: It is the minimum frequency of light needed to cause the photoelectric effect.
16. **Continuous spectrum**: The combination of light of different frequencies in continuous manner is called continuous spectrum.
17. **Line spectrum**: The spectrum of atoms consist of sharp well-defined lines corresponding to definite frequencies is called line spectrum.
18. **Spectroscopy**: The study of emission or absorption spectra is called spectroscopy.
19. **Quantization**: The restriction of a property to discrete values and not continuous values is called quantization.
20. **Quantum mechanics**: The branch of science that takes into account the dual behaviour of matter is called quantum mechanics.
21. **Atomic orbital**: It is the region of space where the probability of finding the electron is maximum.
22. **Quantum numbers**: may be defined as a set of four numbers with the help of which we can get complete information about electron in an atom.

Class : 11th Chemistry
Chapter- 2: Structure of Atom (Part I)

Structure of Atom

Schrodinger Equation

Fundamental Equation was deveoped by Schrodinger as $\hat{H} = \psi \quad \psi \quad \hat{E} =$ where H= Hamiltonian

Quantum Numbers

(i) Principal quantum number (n) :n = 1,2,3,4………… Shell = K, L, M, N……
(ii) Azimuthal Quantum number : For given value of n ,l = 0 to n-1
(iii) Magnetic Quantum number (m) : for subshell with 'l' value m_l=2l+1
(iv) Spin Quantum Number (m_s): $+^1/_2$ (↑), $-^1/_2$ (↓)

Quantum Technical Modal of Atom

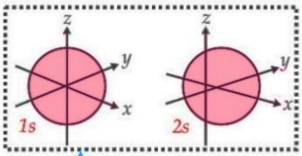
- Dual behaviour of atom i.e., particle and wavelike. De Broglie equation: $\lambda = \frac{h}{mv} = \frac{h}{p}$
- Heisenberg's Uncertainty Principle: It is impossible to determine simultaneously, the exact position and momentum of an electron

Filing of orbitals in atom KE of rejected electron hv = hv0 + 1/2 m e v2

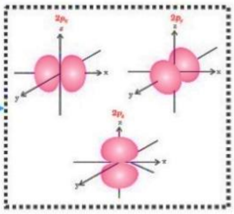
- •Aufbau Principle: In the ground state of atoms, the orbital's are filled according to increasing energies.
- •P auli Exclusion Principle: No2 electrons in an atom can have sae set of four quantum numbers.
- •Hund's rule: Pairing of electronsinthe orbitals belonging to same subshell does not take place until eachelectron belonging to the subshell is singly occupied.

Shapes of orbitals

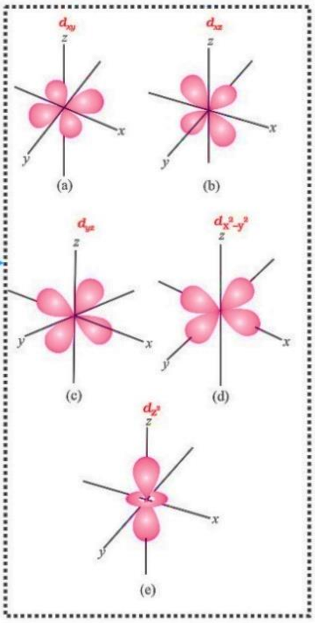
s Orbitals:
Spherically symmetric
Size increases with increase in size in n, ie, 4s>3s>2s>1s



p Orbitals:
Each p Orbitals consists of two sections called lobes on either side of plane passing through the nucleus.

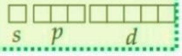


d Orbitals
– "Clover leaf" distribution.
–Two angular nodes.



Electric Configuration of atoms

(i)$s^a p^b d^c$……… notation
(ii)Orbital diagram



Photoelectric Effect it was found By H.Hertz

- It is the phenomenon of ejection of
- electrons from the surface of a
- metal when light of suitable
- frequency strikes on it.

Energy of orbit

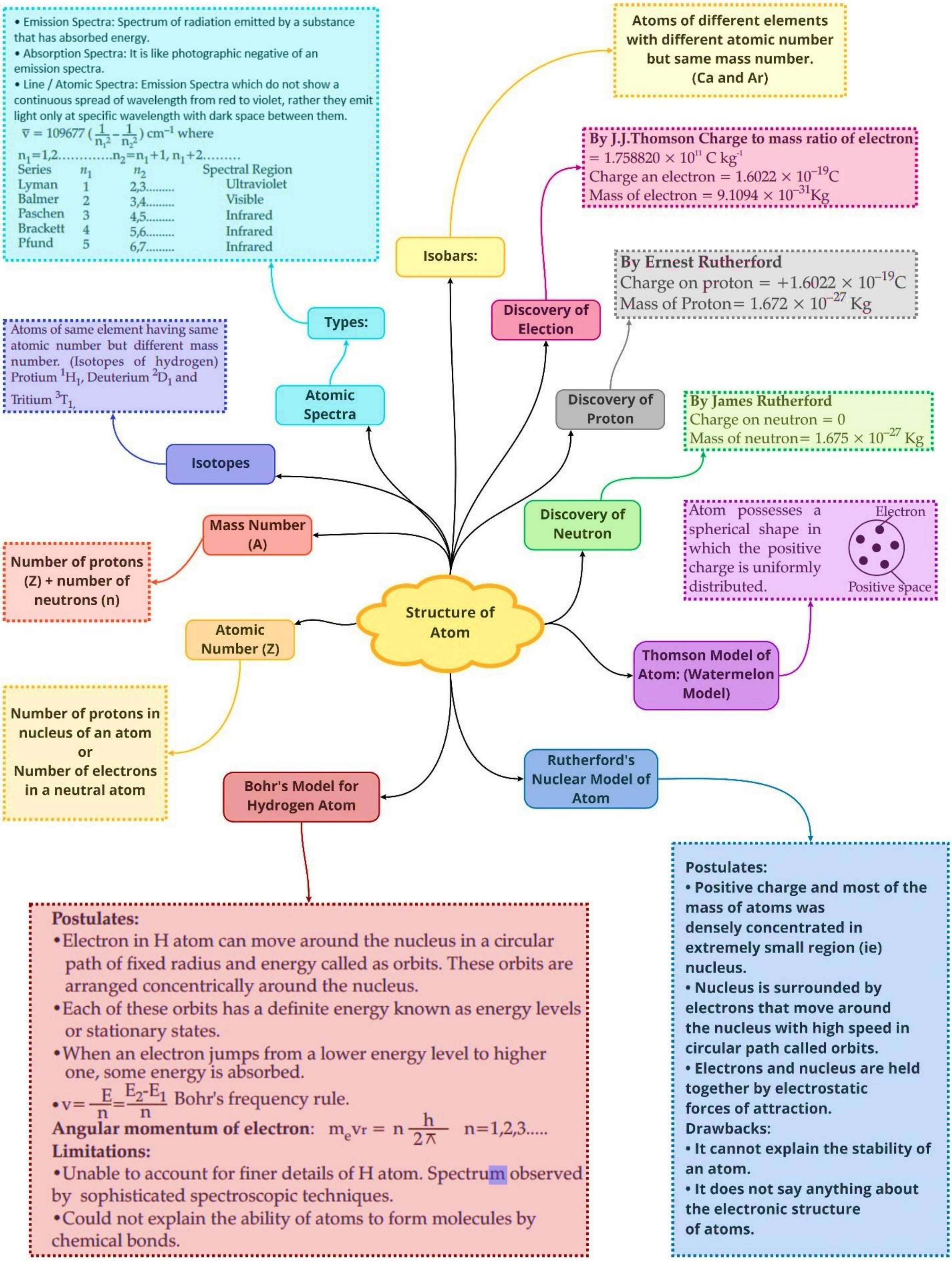
Lower the value of (n+l) for an orbital, lower is its energy.

Developments leading to Bohar's Modal of Atom

Dual nature ie wave like and particle like of the electromagnetic radiation.
- Experimental results regarding atomic spectra.
- Wave nature of electromagnetic radiation: It was given by James Maxwell.

Frequency (v) : Number of waves that pass a given point in one second. Unit – Hertz (Hz), Velocity of light = Frequency × Wave length
Wave number (v) : Number of wavelengths per unit length. Unit – m^{-1}
- Particle nature of electromagnetic radiation: Planck's quantum theory: E = h

Planck's constant (h) = 6.626 × 10^{-34} Js



Structure of Atom

Atomic Spectra

Types:

- Emission Spectra: Spectrum of radiation emitted by a substance that has absorbed energy.
- Absorption Spectra: It is like photographic negative of an emission spectra.
- Line / Atomic Spectra: Emission Spectra which do not show a continuous spread of wavelength from red to violet, rather they emit light only at specific wavelength with dark space between them.

$\bar{\nu} = 109677\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)\text{ cm}^{-1}$ where

$n_1=1,2............n_2=n_1+1, n_1+2........$

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

Isobars:

Atoms of different elements with different atomic number but same mass number. (Ca and Ar)

Discovery of Election

By J.J.Thomson Charge to mass ratio of electron $= 1.758820 \times 10^{11}\text{ C kg}^{-1}$

Charge an electron $= 1.6022 \times 10^{-19}$C

Mass of electron $= 9.1094 \times 10^{-31}$Kg

Discovery of Proton

By Ernest Rutherford

Charge on proton $= +1.6022 \times 10^{-19}$C

Mass of Proton$= 1.672 \times 10^{-27}$ Kg

Discovery of Neutron

By James Rutherford

Charge on neutron = 0

Mass of neutron$= 1.675 \times 10^{-27}$ Kg

Thomson Model of Atom: (Watermelon Model)

Atom possesses a spherical shape in which the positive charge is uniformly distributed.

Isotopes

Atoms of same element having same atomic number but different mass number. (Isotopes of hydrogen) Protium $^1H_1$, Deuterium $^2D_1$ and Tritium $^3T_1$

Mass Number (A)

Number of protons (Z) + number of neutrons (n)

Atomic Number (Z)

Number of protons in nucleus of an atom
or
Number of electrons in a neutral atom

Bohr's Model for Hydrogen Atom

Postulates:

- Electron in H atom can move around the nucleus in a circular path of fixed radius and energy called as orbits. These orbits are arranged concentrically around the nucleus.
- Each of these orbits has a definite energy known as energy levels or stationary states.
- When an electron jumps from a lower energy level to higher one, some energy is absorbed.
- $v=\frac{E}{n}=\frac{E_2-E_1}{n}$ Bohr's frequency rule.

Angular momentum of electron: $m_e vr = n\frac{h}{2\pi}$ n=1,2,3.....

Limitations:

- Unable to account for finer details of H atom. Spectrum observed by sophisticated spectroscopic techniques.
- Could not explain the ability of atoms to form molecules by chemical bonds.

Rutherford's Nuclear Model of Atom

Postulates:

- **Positive charge and most of the mass of atoms was densely concentrated in extremely small region (ie) nucleus.**
- **Nucleus is surrounded by electrons that move around the nucleus with high speed in circular path called orbits.**
- **Electrons and nucleus are held together by electrostatic forces of attraction.**

Drawbacks:

- **It cannot explain the stability of an atom.**
- **It does not say anything about the electronic structure of atoms.**

Important Questions

Multiple Choice questions-

1. Which of the following pair of ions have same paramagnetic moment?

(a) Cu^{+2}, Ti^{+3}

(b) Mn^{+2}, Cu^{+2}

(c) Ti^{+4}, Cu^{+2}

(d) Ti^{+3}, Ni^{+2}

2. The charge to mass ratio of α – particles is approximately …… the charge to mass ratio of protons

(a) Twice

(b) Half

(c) Four times

(d) Six times

3. The frequency of a wave of light is $12 \times 10^{14} s^{-1}$. The wave number associated with this light

(a) 5×10^{-7}m

(b) $4 \times 10^{-8} cm^{-1}$

(c) $2 \times 10^{-7} m^{-1}$

(d) $4 \times 10^{4} cm^{-1}$

4. In a multi – electron atom, which of the following orbitals described by the three quantum numbers will have the same energy in the absence of magnetic acid and electric fields?

(a) n = 1, l = 0, m = 0 (b) n = 2, l = 0, m = 0

(c) n = 2, l = 1, m = 1 (d) n = 3, l = 2, m = 1

(e) n = 3, l = 2, m = 0

(a) (a) and (b)

(b) (b) and (c)

(c) (c) and (d)

(d) (d) and (e)

5. The electronic transitions from n = 2 to n = 1 will produce shortest wavelength in (where n = principal quantum state)

(a) Li^{2+} (b) He^{+}

(c) H (d) H^{+}

6. In a hydrogen atom, if energy of an electron in ground state is 13.6 eV, then that in the 2nd excited state is

(a) 1.51 eV (b) 3.4 eV

(c) 6.04 eV (d) 13.6 eV

7. The credit of discovering neutron goes to

(a) Rutherford

(b) Thomson

(c) Goldstein

(d) Chadwick

8. The maximum number of electrons that can be accommodated in fifth energy level is

(a) 10 (b) 25

(c) 50 (d) 32

9. According to Aufbaus principle, which of the three 4d, 5p and 5s will be filled with electrons first

(a) 4d

(b) 5p

(c) 5s

(d) 4d and 5s will be filled simultaneously

10. A hydrogen atom in its ground state absorbs 10.2 eV of energy. The orbital angular momentum is increased by (Given Planck constant h = 6.6×10^{-34} Jsec)

(a) 1.05×10^{-34} Jsec

(b) 3.16×10^{-34} Jsec

(c) 2.11×10^{-34} Jsec

(d) 4.22×10^{-34} Jsec

11. The ionization enthalpy of hydrogen atom is 1.312×10^{6} J mol^{-1}. The energy required to excite the electron in the atom from n = 1 to n = 2 is

(a) 8.51×10^{5} Jmol-1

(b) 6.56×10^{5} Jmol-1

(c) 7.56×10^{5} Jmol-1

(d) 9.84×10^{5} Jmol$^{-1/sup>}$

12. For principal quantum number n = 4, the total number of orbitals having l = 3 is

(a) 3 (b) 7

(c) 5 (d) 9

13. Maximum number of electrons in a subshell with l = 3 and n = 4 is

(a) 10

(b) 12

(c) 14

(d) 16

14. Which hydrogen-like species will have same radius as that of Bohr orbit of hydrogen atom?
    (a) n = 2, Li^{2+}
    (b) n = 2, Be^{3+}
    (c) n = 2, He^{+}
    (d) n = 3, Li^{2+}
15. The magnetic quantum number specifies
    (a) Size of orbitals
    (b) Shape of orbitals
    (c) Orientation of orbitals
    (d) Nuclear Stability

Very Short:

1. How many total electrons are present in nitrate ion?
2. The nucleus of the atom of an element does not contain a neutron. Name the element and what does its nucleus consists of.
3. What are nucleons?
4. Write electronic configurations of Chromium (At. Np. = 24).
5. Which of the following has the smallest de-Broglie wavelength? O_2, H_2, a proton, an electron
6. How many unpaired electrons are there is a carbon atom in the ground state?
7. What type of spectrum is obtained when light emitted from the discharge tube containing hydrogen gas is analyzed?
8. What is the maximum number of electrons in an atom having n = 3, l = 1 and $s = +\frac{1}{2}$?
9. Name the spectral line in the spectrum of H-atom obtained when an electron jumps from n = 4 to n = 2.
10. Give some examples of electromagnetic radiation.

Short Questions:

1. Enumerate the important characteristics of anode-rays (or positive rays). How this study led to the discovery of proton?
2. What is anode-rays? Illustrate their formation by a diagram.
3. Describe the important properties of cathode-rays. What is concluded about the nature of these rays?
4. What are the main features of Rutherford's model of an atom?
5. What is meant by the dual nature of radiation?
6. Describe the drawback to Rutherford's model of the atom.
7. What is the value of?
    (i) Charge to mass ratio (e/m) of electrons,
    (ii) Charge of electrons,
    (iii) Mass of an electron?

Long Questions:

1. Describe the shape of s – and p – orbitals What do you mean by node or nodal surface?
2. How does the Schrodinger wave equation help to understand the probability of finding the electron near the nucleus? What do you mean by an orbital?
3. How many nucleons are present in an atom Nobelium, No? How many electrons are present in the atom? How many nucleons may be considered neutrons?
4. Complete the following table:

Particle	Atomic No.	Mass No.	No. of electrons	No. of protons	No. of neutrons
Sodium atom	11	—	—	—	12
Aluminum ion	—	27	10	—	—
Chloride ion	—	—	18	—	18
Phosphorus atom	—	31	—	15	—
Cuprous ion	—	—	28	—	35

5. Find the number of protons, electrons an-d neutrons in (a) $13^{27}A^{3+}$

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

Assertion (A): All isotopes of a given element show the same type of chemical behavior.

Reason (R): The chemical properties of an atom are controlled by the number of electrons in the atom.

(i) Both A and R are true and R is the correct explanation of A.
(ii) Both A and R are true but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) Both A and R are false.

2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

Assertion (A): Black body is an ideal body that emits and absorbs radiations of all frequencies.

Reason (R): The frequency of radiation emitted by a body goes from a lower frequency to higher frequency with an increase in temperature.

(i) Both A and R are true and R is the correct explanation of A.

(ii) Both A and R are true but R is not the explanation of A.

(iii) A is true and R is false.

(iv) Both A and R are false.

Case Study Based Question:

1. The atomic theory of matter was first proposed on affirm scientific basis by John Dalton, a British schoolteacher in 1808. His theory, called Dalton's atomic theory, regarded the atom as the ultimate particle of matter Dalton's atomic theory was able to explain the law of conservation of mass, law of constant composition and law of multiple proportion very successfully. However, it failed to explain the results of many experiments. In mid 1850s many scientists mainly Faraday began to study electrical discharge in partially evacuated tubes, known as cathode ray discharge tubes. Electrical discharge carried out in the modified cathode ray tube led to the discovery of canal rays carrying positively charged particles. The characteristics of these positively charged particles are listed below.

1) Unlike cathode rays, mass of positively charged particles depends upon the nature of gas present in the cathode ray tube. These are simply the positively charged gaseous ions.

2) The charge to mass ratio of the particles depends on the gas from which these originate.

3) Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge.

4) The behaviour of these particles in the magnetic or electrical field is opposite to that observed for electron or cathode rays.

The smallest and lightest positive ion was obtained from hydrogen and was called proton. This positively charged particle was characterised in 1919. Later, a need was felt for the presence of electrically neutral particle as one of the constituent of atom. These particles were discovered by Chadwick (1932) by bombarding a thin sheet of beryllium byα-particles. When electrically neutral particles having a mass slightly greater than that of protons were emitted. He named these particles as neutrons. 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 Many different names are given to this model, for example, plum pudding, raisin pudding or watermelon. This model can be visualised as a pudding or watermelon of positive charge with plums or seeds (electrons)embedded into it. An important feature of this model is that the mass of the atom is assumed to be uniformly distributed over the atom. Rutherford and his students (Hans Geiger and Ernest Marsden) bombarded very thin gold foil with α–particles. Rutherford's famous α–particle scattering experiment. The observations of Scattering experiment are as follows-:

(i) most of the α–particles passed through the gold foil undeflected.

(ii) a small fraction of the α–particles was deflected by small angles.

(iii) a very few α–particles (~1 in 20,000) bounced back, that is, were deflected by nearly 180°.

On the basis of observations and conclusions from this experiment, Rutherford proposed the nuclear model of atom. 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.

(1) The atomic theory of matter was first proposed on affirm scientific basis by.

(a) John Dalton
(b) Ernest Rutherford
(c) J. Thomson
(d) Henry Moseley

(2) The cathode rays start from.......... and move towards the ....

(a) Anode, Cathode
(b) Centre, Anode
(c) Cathode, Anode
(d) Cathode, Centre

(3) Negatively charged particles in atoms, called ....

(a) Protons
(b) Electrons
(c) Neutron
(d) Positron

(4) The smallest and lightest positive ion was obtained from..........and was called proton.

(a) Oxygen
(b) Nitrogen
(c) Carbon
(d) Hydrogen

(5) Electrically neutral particles having a mass slightly greater than that of protons, these particles termed as ....

(a) Protons
(b) electrons
(c) Neutron
(d) Positron

2. The presence of positive charge on the nucleus is due to the protons in the nucleus. As established earlier, the charge on the proton is equal but opposite to that of electron. Atomic number (Z) = number of protons in the nucleus of an atom = number of electrons in a neutral atom. 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).

Isobars are the atoms with same mass number but different atomic number for example, $6^{14}C$ and $7^{14}N$. On the other hand, atoms with identical atomic number but different atomic mass number are known as Isotopes. For example, considering of hydrogen atom again, 99.985%of hydrogen atoms contain only one proton. This isotope is called protium (1^1H). Rest of the percentage of hydrogen atom contains two other isotopes, the one containing 1 proton and 1neutron is called deuterium ($^2{}_1D$, 0.015%)and the other one possessing 1 proton and 2neutrons is called tritium ($^1{}_3T$)..the studies of interactions of radiations with matter have provided immense information regarding the structure of atoms and molecules. Niels Bohrutilised these results to improve upon the model proposed by Rutherford. Two developments played a major role in the formulation of Bohr's model of atom. These were:

(i) Dual character of the electromagnetic radiation which means that radiations possess both wave like and particle like properties, and

(ii) Experimental results regarding atomic spectra.

James Maxwell (1870) was the first to give a comprehensive explanation about the interaction between the charged bodies and the behavior of electrical and magnetic fields on macroscopic level. He suggested that when electrically charged particle moves undercalculation, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves called electromagnetic waves or electromagnetic radiation. radiations are characterised by the properties, namely, frequency (ν) and wavelength (λ). The SI unit for frequency (ν) is hertz(Hz, s^{-1}), after Heinrich Hertz. It is defined as the number of waves that pass a given pointing one second. Wavelength should have the units of length and as you know that the SI units of length is meter (m). Since electromagnetic radiation consists of different kinds of waves of much smaller wavelengths, smaller units are used. In vacuum all types of electromagnetic radiations, regardless of wavelength, travel at the same speed, i.e., $3.0 \times 10^8 m\ s^{-1}$ ($2.997925 \times 10^8\ ms^{-1}$, to be precise). This is called speed of light and is given the symbol ‘c‘. The frequency (ν), wavelength (λ) and velocity of light(c) are related by the following equation.

$$c = \nu \lambda$$

The other commonly used quantity specially in spectroscopy, is the wavenumber. It is defined as the number of wavelengths per unit length. Its units are reciprocal of wavelength unit, i.e., m^{-1}. However commonly used unit is cm^{-1}

1) The presence of positive charge on the nucleus is due to the ………… in the nucleus.
   (a) Protons
   (b) Neutrons
   (c) Electron
   (d) Nucleons

2) Atomic Number is denoted by ………..
   (a) A
   (b) Z
   (c) N
   (d) M

3) Atomic Mass number is denoted by …………..
   (a) M
   (b) Z
   (c) N
   (d) A

4) ………… are the atoms with same mass number but different atomic number.
   (a) Isotopes
   (b) Allotropes
   (c) Isobars
   (d) None of above

5) Atoms with identical atomic number but different atomic mass number are known as.
   (a) Isotopes
   (b) Allotropes
   (c) Isobars
   (d) None of above

Answer Key

MCQ Answers:

1. (a) Cu^{+2}, Ti^{+3}
2. (b) Half
3. $4 \times 10^4 cm^{-1}$
4. (d) (d) and (e)
5. (a) Li^{2+}
6. (a) 1.51 eV
7. (d) Chadwick
8. (c) 50
9. (9) 5s
10. (a) 1.05×10^{-34} Jsec
11. (d) $9.84 \times 10^5 J\ mol^{-1}$
12. (b) 7
13. (c) 14
14. (b) n = 2, Be^{3+}
15. (c) Orientation of orbitals

Very Short Answer:

1. No. of electrons in NO_3^- ion

   = No. of electrons on N + No. of electrons on 3 oxygen atoms + one ē

   = 7 + 3 × 8 + 1 = 32 electrons.

2. The nucleus of hydrogen. It contains only one proton.

3. The neutrons and protons present in the nucleus of an atom are collectively called nucleons.

4. Cr = 24 = $1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^6$ $3d^5$, $4s^1$.

5. According to the de-Broglie equation $\lambda = \frac{h}{m \times v}$ for same value of velocity $\lambda \propto \frac{1}{m}$

   ∴ O_2 molecule has shortest wavelength.

6. C = 6 = $1s^2$, $2s^2$, $2p^1x$ $2p^1y$. There are only two unpaired electrons.

7. Emission line spectrum.

8. Three electrons (one each in $3p_x$' $3p_y$', $3p_z$').

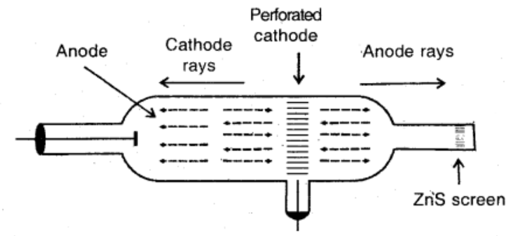
9. Balmer Series.

10. Y-rays, X-rays, UV-rays, visible rays, radio waves, etc.

Short Answer:

1. **Ans:** The mass of positive particles which constitute these rays depend upon the nature of the gas in the tube. The charge/mass (e/m) ratio of anode-rays is not constant but depends upon the nature of gas in the tube. The value of e/m is greatest for the lightest gas, hydrogen the electric charge on a lightest positively charged particle from hydrogen gas was found to be exactly equal in magnitude but opposite in sign to that of the electron. This lightest positively charged particle from hydrogen gas was named the proton. The mass of a proton is almost 1836 times that of the electron.

2. **Ans:** Anode-rays. If a perforated cathode is used in the discharge tube experiment, it is found that a certain type of radiation also travels from anode to cathode. These are called anode rays or positive rays.



Production of anode rays

3. **Ans:** The cathode rays possess the following properties:

1. Travel in straight lines perpendicular to the surface of the cathode.
2. Consists of material particles.
3. Have got the heating effect.
4. Consists of negatively charged particles.
5. Produce X-rays when they strike against hard metals like copper, tungsten, platinum, etc.
6. Produce fluorescence when they strike glass or certain other materials like zinc sulfide.
7. Penetrate through thin aluminum foils and other metals.
8. Affect the photographic plates.

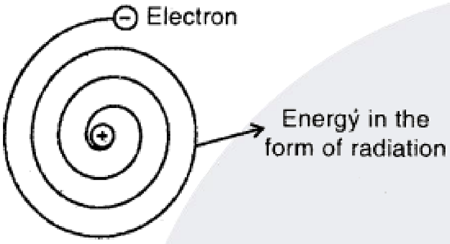
4. **Ans:** The main features of this model are:

1. Atom is spherical and consists of two parts: Nucleus and extra-nuclear part.
2. The entire mass and entire positive charge are concentrated in a very small region at the center known as the nucleus.
3. The space surrounding the nucleus known as the extra-nuclear part is negatively charged so an atom as a whole is neutral.
4. Most of the extra-nuclear part is empty.
5. The electrons are not stationary but are revolving around the nucleus at very high speeds like planets revolving around the Sun.

5. **Ans:** The fact that light energy is carried in terms of packets of energy (i.e., photons) as suggested by Planck's theory means that light has a particle character. At the same time, the fact light has a wave character. These experimental facts led Einstein to suggest that light has a dual character, i.e., it behaves both like a wave and like a particle.

6. **Ans:** The main drawback is that it could not explain the stability of an atom. Maxwell has shown that when electric charge is subjected to acceleration, it emits energy in the form of radiations. In Rutherford's model of the atom, electrons are orbiting the nucleus and hence the direction of their velocity is constantly changing, i.e., electrons are accelerating.

   This will cause the electrons will have lesser and lesser energy and will get closer and closer to the nucleus until at last, it spirals into the nucleus and thus does not provide a stable model of the atom.



7. **Ans:** J. Thomson determined the value of e/m for electron by the study of deflection of electron beam under the simultaneous influence of electric and magnetic field perpendicular to each other, the e/m value is 1.76 × 108 coulomb per gram of electrons

   The charge of electrons was measured by Millikan in 1909 by his famous 'oil drop' experiment. It was found to be 1.60 × 10-19 coulombs.

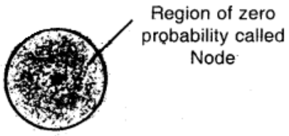
   The mass of electrons is 9.1 × 10-28 g.

Long Answer:

1. **Ans: Shapes of Orbitals:**

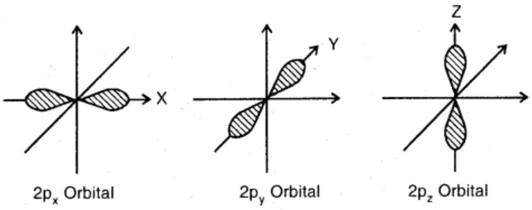
   s-orbitals: These are spherically symmetrical and non-directional. Shapes of 1s and 2s orbitals are shown in Fig. The effective volume of 2s orbital is larger than is orbital. Another important feature of 2s orbital is that there is a spherical shell within 2s (region without dots) where the probability of finding the electron is zero. This is called a node or a nodal surface. There are (n - 1) nodes in an s-orbital (where n is the energy level).

1s-Orbital



2s-Orbital

p-orbitals: There are three p-orbitals designated as px', py' or pz' which are oriented along the three mutually perpendicular axis x, y, and 2. Each, orbital consists of two lobes symmetrical about the particular axis and has a dumbbell shape. The two lobes are separated by a nodal plane.



Shapes of three 2p orbitals

The two lobes of each orbital are separated by a plane having x zero electron density. This plane is known as a nodal plane.

2. **Ans: Probability Picture of Electrons:**

   Schrodinger incorporated the requirements of the uncertainty principle and de Broglie's concept of matter waves and proposed a mathematical equation to describe the behavior of an electron in an atom. The equation was known as the Schrodinger wave equation.

   The Schrodinger wave equation is:

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$$

   where x, y, and z are three space coordinates,

   m is the mass of the electron,

   h is Planck's, constant

   E is the total energy and V is the potential energy of the electron, φ (Greek letter psi) is the amplitude of the wave, called wave function, $\frac{\partial 2\psi}{\partial x2}$ refers to the second derivative of φ with respect to x only and so on.

   The solution of this equation gave the mathematical expression which gives information about the various energy states and other measurable properties such as the radiation frequencies emitted or absorbed for the hydrogen atom. The solutions of the Schrodinger wave equation are called wave functions and are denoted by the symbol φ.

   The physical significance of wave function: In the physical sense φ gives the amplitude of the wave associated with the electron. We know that in the case of light waves, the square of the amplitude, of the wave at a point is proportional to the intensity of light. Extending the same concept of electron wave motion, the square of the wave function, $\varphi 2$ may be taken as the intensity of electrons at any point.

In other words, φ^2 determines the probability density. Thus, φ^2 has been called the probability density and φ the probability amplitude. Thus, the solutions of the Schrodinger wave equation replace the discrete energy levels or orbits proposed by Bohr and led to the concept of the most probable regions in space in terms of $\varphi 2^2$.

A large value of φ^2 means a high probability of finding the electron at that place and a small value of φ^2 means low probability. If φ^2 is almost zero at a particular point, it means that the probability of finding the electron at that point is negligible. Therefore, the wave mechanics approach gives meaningful wave functions which describe the position and energy levels of electrons in an atom.

Concept of Orbital: An orbital is a region in space around the nucleus where the probability of finding the electrons is maximum.

3. **Ans:** Nucleons = 254, electrons = 102 and neutrons 254 - 102 = 152.

4. **Ans:**

Particle	Atomic No.	Mass No.	No. of electrons	No. of protons	No. of neutrons
Sodium atom	11	23	11	11	12
Aluminum ion	13	27	10	13	14
Chloride ion	17	35	18	17	18
Phosphorus atom	15	31	15	15	16
Cuprous ion	29	64	28	29	35

5. **Ans:**

Particle	Mass No.	Atomic No.	Protons	No. of Electrons	Neutrons
Oxygen	16	8	8	8	8
Sodium ion	23	11	11	10	12
Bromine	80	35	35	35	45

Assertion Reason Answer:

1. (i) Both A and R are true and R is the correct explanation of A.
2. (ii) Both A and R are true but R is not the explanation of A.

Case Study Answer:

1. **Ans:**
   (1) (a) John Dalton
   (2) (c) Cathode, Anode
   (3) (b) electrons
   (4) (d) Hydrogen
   (5) (c) Neutron
2. **Ans:**
   (1) (a) Protons
   (2) (b) Z
   (3) (d) Z
   (4) (c) Isobars
   (5) (a) Isotopes

❖ ❖

Some Basic Concepts of Chemistry

3

Introduction

Classification of elements was proposed in order to study all the elements in a systematic manner. In this Unit, we shall study the development of the Periodic Law and the Periodic Table. Mendeleev's Periodic Table was based on atomic masses. Modern Periodic Table arranges the elements in the order of their atomic numbers in seven horizontal rows (periods) and eighteen vertical columns (groups or families).

Why Do We Need Classification?

Elements are the basic units of all types of matter. At present, 118 elements are known. With such a large number of elements, it is very difficult to study individually the chemistry of all these elements and their number of compounds. So, to make the study of chemistry simpler, scientists searched for a systematic way to organise their knowledge by classifying the elements. Main aim behind this classification was to keep the elements of same properties together, so that by studying one element out of that group, we can have general idea about the properties of all the elements in that group.

Periodic Table

Periodic table may be defined as the tabular arrangement of elements in such a way that the elements having same properties are kept together.

Dobereiner's Triads Law

1st attempt towards the classification of elements was made by Johann W. Dobereiner in 1817. He arranged elements in the groups of three and in such a way that the atomic weight of middle element was equal or nearly equal to the average of atomic weights of other two elements.

	ELEMENTS	SYMBOL	ATOMIC MASS
1	Lithium	Li	6.9
	Sodium	Na	23
	Potassium	K	39
2	Calcium	Ca	40.1
	Strontium	Sr	87.6
	Barium	Ba	137.3
3	Chlorine	Cl	35.5
	Bromine	Br	79.9
	Iodine	I	126.9

Drawback: Only limited triads were arranged in this pattern.

Newland's Law of Octaves

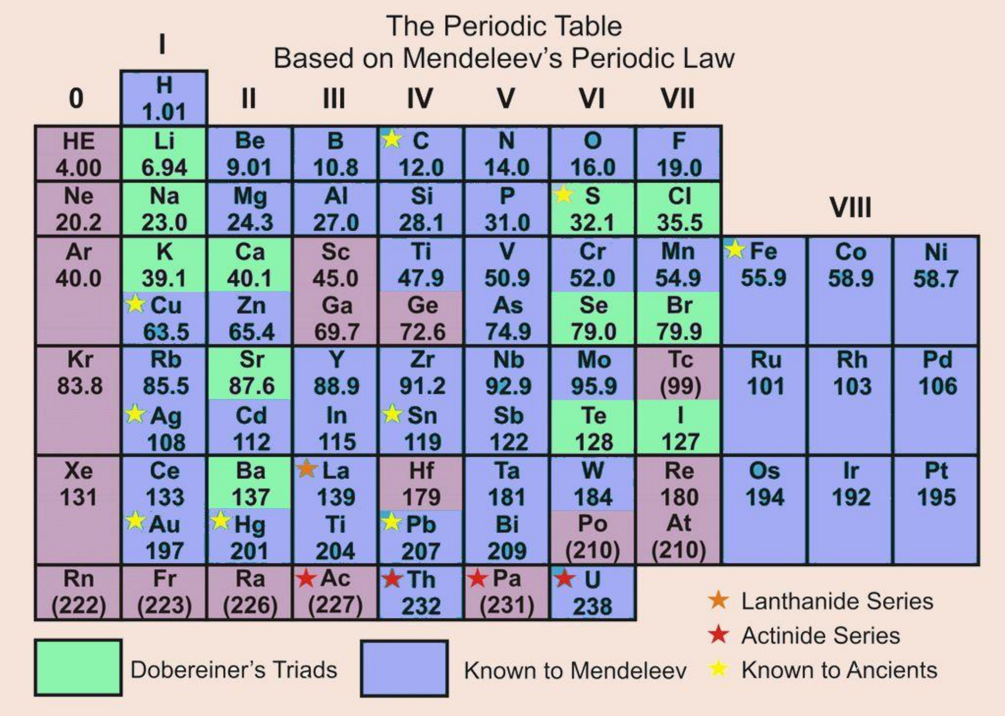
In 1865, John Newland observed that in a series of elements arranged in the increasing order of atomic weights, 1st and 8th elements have same properties. Now, a days, 1st and 9th elements have same properties in that series because noble gases were discovered late.

1	2	3	4	5	6	7	8
Li	Be	B	C	N	O	F $\boxed{\text{Ne}}$	Na
9	10	11	12	13	14	15	16
Mg	Al	Si	P	S	Cl $\boxed{\text{Ar}}$	K	Ca

Mendeleev's Periodic Table

"The physical and chemical properties of elements are a periodic function of atomic weights".

Mendeleev arranged elements in horizontal rows and vertical columns of a table in order of their increasing atomic weights in such a way that the elements with similar properties occupied the same vertical column or group. Vertical Colums are called groups which are numbered I to VIII group, each group is further subdivided into sub groups A and B. Horizontal rows are called **periods**.



The Periodic Table
Based on Mendeleev's Periodic Law

0	I	II	III	IV	V	VI	VII	VIII		
	H 1.01									
HE 4.00	Li 6.94	Be 9.01	B 10.8	★ C 12.0	N 14.0	O 16.0	F 19.0			
Ne 20.2	Na 23.0	Mg 24.3	Al 27.0	Si 28.1	P 31.0	★ S 32.1	Cl 35.5			
Ar 40.0	K 39.1	Ca 40.1	Sc 45.0	Ti 47.9	V 50.9	Cr 52.0	Mn 54.9	★ Fe 55.9	Co 58.9	Ni 58.7
	★ Cu 63.5	Zn 65.4	Ga 69.7	Ge 72.6	As 74.9	Se 79.0	Br 79.9			
Kr 83.8	Rb 85.5	Sr 87.6	Y 88.9	Zr 91.2	Nb 92.9	Mo 95.9	Tc (99)	Ru 101	Rh 103	Pd 106
	★ Ag 108	Cd 112	In 115	★ Sn 119	Sb 122	Te 128	I 127			
Xe 131	Ce 133	Ba 137	★ La 139	Hf 179	Ta 181	W 184	Re 180	Os 194	Ir 192	Pt 195
	★ Au 197	★ Hg 201	Ti 204	★ Pb 207	Bi 209	Po (210)	At (210)			
Rn (222)	Fr (223)	Ra (226)	★ Ac (227)	★ Th 232	★ Pa (231)	★ U 238				

★ Lanthanide Series
★ Actinide Series
★ Known to Ancients
🟩 Dobereiner's Triads
🟦 Known to Mendeleev

Defects in Mendeleev's Table-

i. **Position of hydrogen**: Position of hydrogen was not justified.

ii. **Position of isotope**: Isotopes should be placed separately according to periodic law. But actually one place was given to all isotopes of an element.

iii. **Cause of periodicity**: Mendeleev could not explain why elements exhibit a periodicity in their properties when arranged in the order of increasing atomic weight.

iv. **Anomalous pairs of elements**: Some anomalous pairs were present in table. As Tellurium (128 u) comes in VI group before Iodine (127 u).

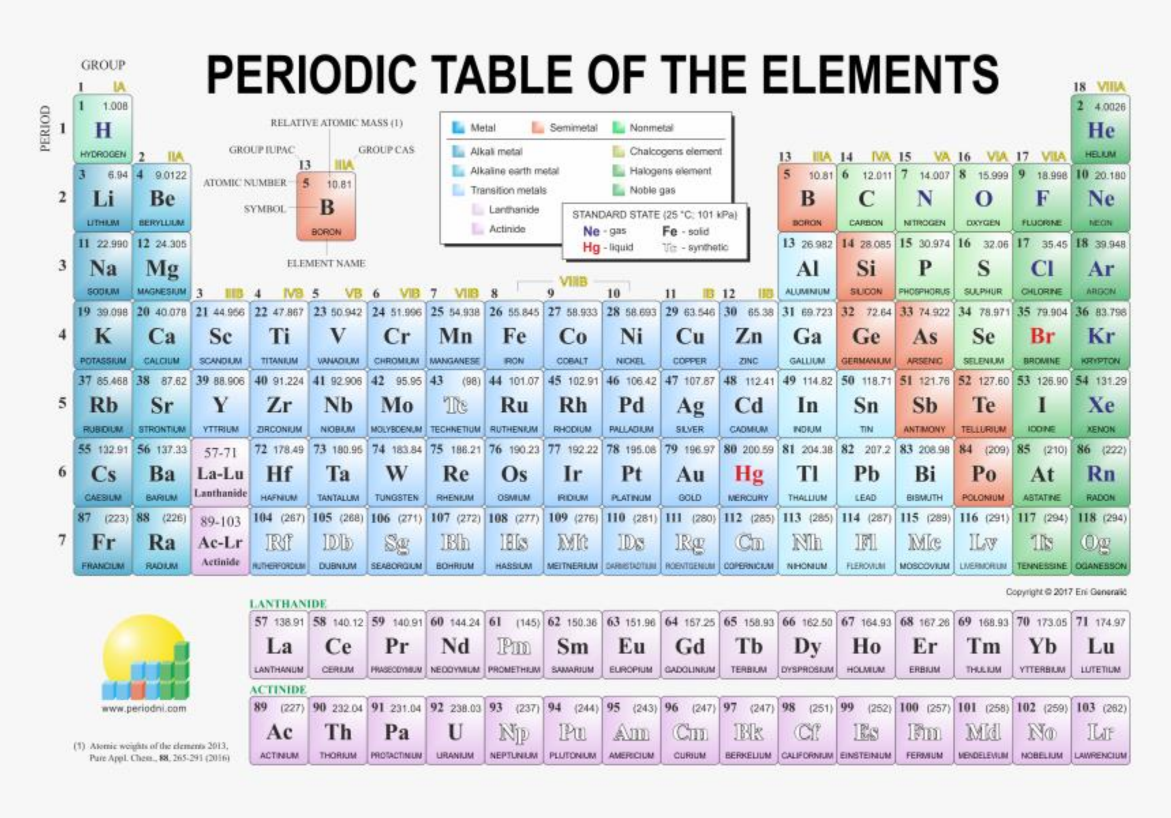
Moseley's Periodic Table

"The physical and chemical properties are the periodic function of their atomic numbers".

The long form of periodic table, also called Modem Periodic Table, is based on Modern periodic law. In this table, the elements have been arranged in order of increasing atomic numbers.

A modern version, the so-called "**long form**" of the **Periodic Table** of the elements, is the most convenient and widely used. The horizontal rows are called periods and the vertical columns, groups. Elements having similar outer electronic configurations in their atoms are arranged in vertical columns, referred to as groups or families. According to the recommendation of International Union of Pure and Applied Chemistry (IUPAC), the groups are numbered from 1 to 18 replacing the older notation of groups IA … VIIA, VIII, IB … VIIB and 0.

There are altogether seven periods. The period number corresponds to the highest principal quantum number (n) of the elements in the period. The first period contains 2 elements. The subsequent periods consists of 8, 8, 18, 18 and 32 elements, respectively. The seventh period is incomplete and like the sixth period would have a theoretical maximum 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.



The IUPAC names are derived by using roots for three-digit atomic number of the elements.

Digit	Iupac Name	Symbol
0	nil	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

A systematic nomenclature be derived directly from the atomic number of the element using the numerical roots for 0 and numbers 1-9. The roots are put together in order of digits which make up the atomic number and "ium" is added at the end. The IUPAC names for elements with Z above 100 are shown below:

Atomic Number	Name according to IUPAC nomenclature	Symbol	IUPAC Official Name	IUPAC Symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnihexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununnillium	Unn	Darmstadtium	Ds
111	Unununnium	Uuu	Rontgenium	Rg
112	Ununbium	Uub	Copernicium	Cn
113	Ununtrium	Uut	Nihonium	Nh
114	Ununquadium	Uuq	Flerovium	Fl
115	Ununpentium	Uup	Moscovium	Mc
116	Unuhexium	Uuh	Livermorium	Lv
117	Ununseptium	Uus	Tennessine	Ts
118	Ununoctium	Uuo	Oganesson	Og

Division of Elements into Blocks

s-block: 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.

Characteristics of s-Block elements,

i. Except Be and Mg, all impart characteristic colour to the flame.

ii. These have low ionisation energy.

iii. These are highly reactive.

iv. These are the highly electropositive elements.

v. All the elements are soft metals.

vi. They have low melting and boiling points.

p-block: 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.

Characteristics of p-Block elements,

1. The compounds of p-block elements are generally covalent although their ionic character increases down the group.

2. From left to right 13 to 18, reducing character decreases.
3. The p-block elements generally show more than one oxidation state.
4. The reactivity of elements in a group generally decreases downwards.
5. At the end of each period is a noble gas element with a closed valence shell ns^2 np^6 configuration.

d-block: 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 $(n-1)\ d^{1-10}ns^{0-2}$.

Characteristics of d-Block elements:

1. They are all metals with high melting and boiling points.
2. The compounds of the elements are generally paramagnetic in nature.
3. They mostly form coloured ions, exhibit variable valence (oxidation states).
4. They are of tenly used as catalysts.
5. These elements have high melting point.

f-block: 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).

Characteristics of f-Block elements:

1. All actinoids are radioactive. Elements after uranium are known as transuranium element.
2. They form coloured compounds.
3. These two series of elements are called Inner Transition Elements (f-Block Elements).
4. They are all metals. Within each series, the properties of the elements are quite similar.
5. They generally have high melting and boiling points.

Periodic Properties

The properties which generally have a regular trend along a group or period are called periodic properties. These are as given below:

- Atomic size
- Ionisation energy
- Electron gain enthalpy
- Electronegativity

i. **Atomic Size**: Atomic Radius is the distance from the centre of the nucleus to the outermost shell containing electron.

Ionic Radius: The ionic radii can be estimated by measuring the distances between cations and anions in ionic crystals. In general, the ionic radii of elements exhibit the same trend as the atomic radii.

Cation: The removal of an electron from an atom results in the formation of a cation. The radius of cation is always smaller than that of the atom.

Anion: Gain of an electron leads to an anion. The radius of the anion is always larger than that of the atom.

ii. **Ionization energy**: It is the amount of energy required to remove the outer most electron from an isolated atom in its gaseous state. It is the measured in the unit of kJ/mole. It is denoted by $(\Delta_i H)$.

$$M(g) - e^- \longrightarrow M^+(g)$$

iii. **Electron gain enthalpy**: It is the enthalpy change when an electron is added to the gaseous neutral atom. Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion. It is the measured in the unit of kJ/mole. It is denoted by $(\Delta_{eg}H)$.

$$X(g) + e^- \longrightarrow X^-(g)$$

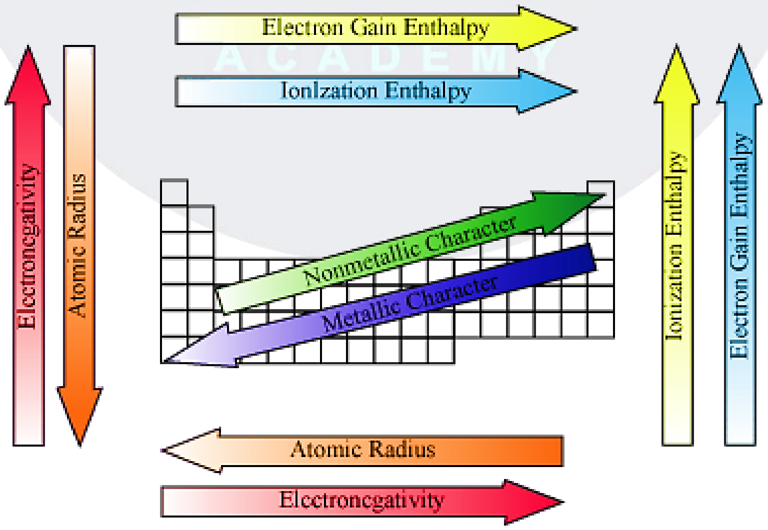
iv. **Electronegativity**: Electronegativity is a measure of the tendency of an element to attract bonded electron pair towards itself in a covalently bonded molecule.

Periodic Trends in Chemical Properties along a Period

1. **Metallic character**: It decreases across a period, maximum on the extreme left (alkali metals).
2. **Non-metallic character**: It increases along a period, from left to right.
3. **Atomic Size**: It decreases across a period.
4. **Ionisation energy**: It increases along a period.
5. **Electron gain enthalpy**: It increases along a period.
6. **Electronegativity**: It increases along a period.
7. **Basic nature of oxides**: It decreases from left to right in a period.
8. **Acidic nature of oxides**: It increases from left to right in a period.

Variation in Chemical Properties along a Group

1. **Metallic character**: Generally increases because increase in atomic size and hence decrease in the ionizatiorn energy of the elements in a group from top to bottom.
2. **Non-metallic character**: It generally decreases down a group. As electronegativity of elements decreases from top to bottom in a group.
3. **Atomic Size**: It increases along a group.
4. **Ionisation energy**: It decreases across a period.
5. **Electron gain enthalpy**: It decreases across a period.
6. **Electronegativity**: It decreases across a period.
7. **Basic nature of oxides**: Since metallic character or electropositivity of elements increases in going from top to bottom in a group basic nature of oxidise naturally increases.
8. **Acidic character of oxides**: It generally decreases as non-metallic character of elements decreases in going from top to bottom in a group.
9. **Reactivity of metals**: It generally increases down a group. Since tendency to lose electron increases.



Historical Development of Periodic Table

Periodic table may be defined as the table which classified all the known elements in accordance with their properties in such a way that elements with similar properties are grouped together in the same vertical column and dissimilar elements are separated from one another.

Doebereiner's Triad

Group	Elements and their Atomic Mass			Arithmetic Mean of Atomic mass
A	Lithium (Li)	Sodium (Na)	Potassium (K)	$\frac{7.0+39.0}{2}=23.0$
	7.0	23.0	39.0	
B	Calcium (Ca)	Strontium (Sr)	Barium (Ba)	$\frac{40.0+137.0}{2}=88.5$
	40.0	87.5	137.0	
C	Chlorine (Cl)	Bromine (Br)	Iodine (I)	$\frac{35.0+127.0}{2}=81.0$
	35.0	80.0	127.0	
	55.8	58.9	58.6	

The first attempt towards the classification of elements was made by Johann Wolfgang Doebereiner, a German chemist in 1817.

He arranged similar elements in groups of three and showed that their atomic weights were either nearly the same or the atomic weight of the middle element was approximately the arithmetic mean of the other two. These group of three elements were called Doebereiner's Triads and this generalisation was called Law of triads.

Drawback

The concept of triads could be applied only to a limited number of elements.

Newlands's law of octaves

In1865 ,an English chemist, John Alexander Newlands's observed at that:

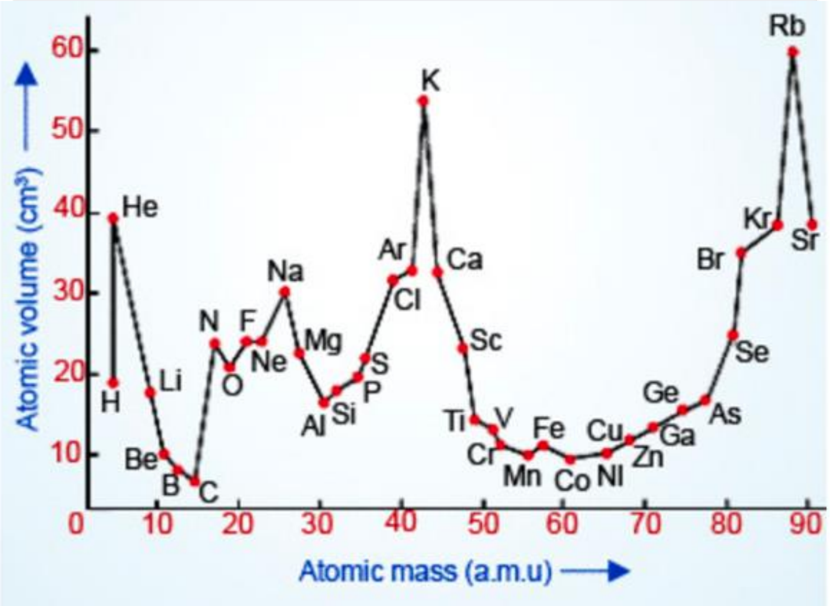
When the lighter elements were arranged in order of their increasing atomic weights ,the properties of every 8th elements were similar to those of first one like the eighth note of a musical scale.This is called as Newlands's law of octaves.

Drawback

1) It was applicable to only lighter elements having atomic weights up to 40 u.

2) With the discovery of noble gases, the properties of the 8th element were no longer similar to those of the first one.

Lothar Meyer arrangement



In 1869, Lothar Meyer, a German chemist, studied the physical properties of various element.

He Plotted a graph between the atomic volume and atomic weights of the elements and observed that the elements with similar properties occupied similar position on the curve.

1) The most strongly electropositive alkali metal occupies the peaks on the curve.
2) The less strongly electropositive alkaline earth metals occupy the descending position on the curve.
3) The most electronegative elements i.e. halogens occupy the ascending position on the curve.

Lothar Meyer proposed that the physical properties of the elements are a periodic function of the atomic weights.

He arranged the elements in the tabular form in order of their increasing atomic weights.

Electronic configuration Of Elements

(1) The names are derived directly from the atomic numbers using numerical root for 0 and numbers from 1-9 and adding the suffix ium. The roots for the numbers 0-9 are:

Digit	0	1	2	3	4	5	6	7	8	9
Root	nil	un	bi	Tri	quad	pent	hex	sept	oct	enn
Abbreviation	n	u	b	t	q	p	g	s	o	e

(2) In certain cases, the names are shortened.bi ium and tri ium are shortened to bium and trium and enn nil shortened to ennil.

(3) The symbol of the element is then obtained from the first letters of the roots of numbers which make up the atomic number of the element.

An electron in an atom is characterised by a set of four Quantum numbers (n, l, m and s) and the Principal quantum number (n) defines the main energy level known as the shell.

Location of any element in the periodic table tells us the quantum number (n and l) of the last orbital filled.

Electronic configuration of elements in period

Each period in the periodic table indicates the value of n for the outermost or the valence shell. The total number of elements in each period is twice the number of orbitals available in the energy level that is being filled.

(1) The first period corresponds to the filling of electrons in the first energy shell i.e. (k shell),n=1.Since this energy shell has only 1 orbital i.e. 1s which can accommodate only 2 electrons, therefore, first period has only 2 elements.

(2) The second period corresponds to the filling of electrons in the second energy shell (L shell) i.e. n=2.This shell has 4 orbitals(one 2s and three 2p) which can accommodate 8 electrons, therefore second period contains 8 electron. It starts with Lithium (Z=3) and ends at neon (Z= 10).

(3) The third period corresponds to the filling of electron in the third shells, i.e. n=3.This shell has 9 orbitals (one 3s, three 3p and five 3d) .3d orbital have even higher energy than 4s orbital. Therefore 3d orbitals are filled only after filling of 4s orbital. Third period involves the filling of only 4 orbitals(one 3s and three 3p) and thus contains 8 elements. It starts with sodium(Z=11) and ends at argon (Z= 18).

(4) The Fourth period corresponds to the filling of electrons in the fourth energy level, n=4. It starts with potassium(Z=19) and ends at calcium (Z= 20).

After the filling of 4s orbitals, the filling of five 3d orbitals begins since the energy of 3d orbital is lower than those of 4p orbitals but higher than that of 4s orbital. The filling of 4d and 4f orbital does not occur in this period since their energies are higher than that of even 5s orbital. The filling of the 3d orbital starts from scandium(Z= 21) and ends at Zinc(Z= 30).These 10 elements constitute the 3d transition series.

The filling of 4p orbital begins at gallium(Z=31)and ends at krypton(Z=36) which has the outer electronic configuration as 4s2 3d10 4p6 .In the 4th period, the filling of only 9 orbitals(one 4s, five 3d and three 4p) occurs which can accommodate at the maximum 18 electrons. Therefore 4th period contain 18 electrons from potassium to Krypton.

(5) The fifth period also contains 18 elements since only 9 orbitals (one 5s, five 4d and three 5p) are available for filling with electrons. It begins with rubidium(Z= 37) in which one electron enters 5s orbital. After the

filling of 5s orbital, the filling of 4d orbital starts at yttrium (Z=39) and ends at cadmium (Z= 48).These ten elements constitute 4d transition series. Filling of 5p orbitals starts at indium (Z= 49) and ends at xenon (Z=54).

(6) The sixth period corresponds to the filling of 6th energy level i.e. n= 6.Only 16 orbitals(one 5s, five 4d and three 5p) are available for filling with electrons, therefore 6th period contains 32 elements. It begins with caesium(Z=55) in which one electron enters the 6s orbital and ends up with radon(Z=86) in which the filling of 6p orbital is complete. After the filling of 6s Orbital, the next electron enters the 5d orbital and therefore the filling of seven 4f orbitals begins with Cerium(Z=58) and ends up with lutetium(Z=71).These 14 elements constitutes the first inner transition series called lanthanides or lanthanoids.

Filling of 5d orbitals which started at lanthanum continuous from hafnium(Z=72) till it is filled at mercury(Z=80). These 10 elements constitutes the 5d- transition series. After the filling of 5d orbitals, the filling of 6p orbitals starts at thallium(Z=81) and ends at the radon (Z=86).

(7) The seventh period corresponds to filling of 7th energy shells i.e. n=7. It also contain 32 elements corresponds to the filling of 16 orbitals(one 7s, seven 5f, five 6d and three 7p).

After the filling of 7s orbital, the next two electrons enters the 6d orbitals and therefore the filling of seven 5f orbitals begin with proactinium(Z=91) and ends up with lawrencium(Z=103).

Thorium does not have any electron in the 5f orbital, yet get it is considered to be a f block element since its properties resemble more the f block element than the d block elements. These 14 elements from thorium(Z=90) to lawrencium(Z=103) constitute the second (or 5f) inner transition series which is called as actinides are actinoids.

Filling of 5d orbitals which started at actinum(Z=89) continues till it is completed at these Uub(Z=112).These 10 elements constitute the 6d transition series. The filling of 6d, orbital the filling of 7p orbitals begins at Uut (Z= 118) which ends at Uut (Z=118) which belongs to noble gas family.

The first three periods containing 2,8,8 elements and are known as short periods while the next three periods containing 18 ,18, 32 elements are called Long periods

Group wise electronic configuration

The elements in the same group or vertical column have similar valence shell electron electronic configuration i.e. they have the same number of electrons in the outer orbitals and hence have similar properties. Elements of group 1 all have ns1 valence shell electronic configuration. Elements of group 17 all have ns2 np5 valence shell electronic configuration.

Prediction of period, group and block of a given element

The period of an element corresponds to the principal quantum number of the valence shell.

The block of an element corresponds to the type of orbital which receive the last electron.

The group of an element is predicted from the number of electrons in the valence shell or/and penultimate shell as follows:

a) For s block elements, group number is equal to the number of valence electrons.

b) For p block elements, group number is equal to 10+number of electrons in the valence shell.

c) For d block elements, group number is equal to the number of electrons in a (n-1) sub shell + the number of electrons in valence shell.

Question: Write the electronic configuration of the element with atomic number 29. Predict the period, group number and block to which it belongs.

Answer: Z = 29 $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

Elements receive the last electron in the 3d orbital; therefore, it belongs to d block elements and its group number = No. of electrons in the penultimate shell and valence shell = 10+ 1 =11

The period of the element = No. of principal quantum number of the valence shell = 4th

Summary-

1. **Periodic table**: Arrangement of elements in the increasing order of atomic number such that elements with similar properties fall under same vertical column.
2. **Group**: A vertical column of elements in the periodic table.
3. **Period**: A horizontal row of elements in the periodic table.
4. **Long form of periodic table** has 18 groups and 7 periods. Sixth period is the longest and first period is the smallest.
5. **s-Block elements**: Elements of groups 1 and 2. Their general valence shell electronic configuration is ns^{1-2}.
6. **p-Block elements**: Elements of groups 13, 14, 15, 16, 17 and 18. Their general valence shell electronic configuration is ns^2np^{1-6}.
7. **d-Block elements**: Elements of groups 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12. Also known as transition elements. Their general valence shell electronic configuration is $(n-1)d^{1-10}\ ns^{1-2}$. $_{46}Pd$ is exception ($4d^{10}\ 5s^0$).
8. **f-Block elements**: The two horizontal rows of elements at the bottom of the table. Also known as inner transition elements. Their general valence shell electronic configuration is $(n-2)f^{1-14}\ (n-1)d^{0-1}\ ns^2$.
9. **Covalent radius**: Half of the internuclear distance between two atoms of the element held by a single covalent bond.
10. **Van der Waal's radius**: Half of the internuclear distance between two nearest atoms belonging to two adjacent molecules in solid state.
11. **Metallic radius**: Half of the internuclear distance between two nearest atoms in the metallic lattice.
12. **Isoelectronic ions**: The ions having same number of electrons but different nuclear charge.

    Example: (i) N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+}; (ii) P^{3-}, S^{2-}, Cl^-, K^+, Ca^{2+}, Sc^{3+}
13. Among isoelectric ions, greater the nuclear charge smaller is the size.
14. **Ionization enthalpy**: The minimum amount energy required to remove the outermost electron from an isolated gaseous atom of the element.
15. Ionization enthalpy increases along the period and decreases down the group.
16. Be, Mg, N, P and noble gases have exceptionally high values of ionization enthalpies due to their stable electronic configurations.
17. **Electron gain enthalpy**: The enthalpy change taking place when an electron is added to an isolated gaseous atom of the element.
18. Electron gain enthalpy becomes more negative as we move along the period and becomes less negative down the group.
19. Successive electron gain enthalpies are always positive.
20. Helium has the highest value of ionization enthalpy in periodic table.
21. Chlorine has the highest negative electron gain enthalpy in periodic table.
22. **Electronegativity**: It is the tendency of an atom in a molecule to attract towards itself the shared pair of electrons.
23. Fluorine is the most electronegative element whereas Caesium is the least electronegative element in periodic table.
24. Unlike ionisation energy and electron affinity, electronegativity is the property of atom of an element in combined state.

25. Electropositive or metallic character is related to the ionisation energy of the element. The elements having low I.E. are more electropositive or more metallic in character.
26. **Valence** of an element belonging to s or p-block is either equal to the number of valence electrons or eight minus the number of valence electron.
27. The chemical reactivity is maximum at the two extreme ends of the periodic table and is least in the centre.
28. Among alkali metals reactivity increases on descending the group while among halogens the reactivity decreases on descending the group.
29. The basic character of oxides decreases while the acidic character increases on going from left to right in a period.
30. Oxides of metals are generally basic while that of non-metals are acidic in nature.
31. The similarity between a pair of elements in period second and third located diagonally in the periodic table is called the **diagonal relationship**.

Class : 11th Chemistry
Chapter- 3: Classification of Elements and Periodicity in Properties

Classification of Elements and Periodicity in Properties

Periodic Trends in Properties of Elements

Properties	Group	Period
(a) Atomic Radius : Distance from the centre of the nucleus to the outermost shell containing electrons.	Increases	Decreases
(b) Electron Gain Enthalpy : Energy released when a neutral isolated gabelous atom accepts an electron from anion.	Becomes less negative	Becomes more negative
(c) Ionization Energy: The minimum amount of energy required to remove the electron from the outmost orbit of an isolated atom in gaseous state.	Decreases	Increases
(d) Electronegativity : Tendency of an atom to attract the shared pair of electrons towards it "Group"self.	Decreases	Increases
(e) Electron Affinity	Decreases	Increases
(f) Valency: Number of univalent atoms which combine with an atom of given element.	No Change	Increase from 1 to 4 and then decrease from 4 to 0.
(g) Metallic Character:	Increases	Decreases
(h) Non–Metallic Character:	Decreases	Increases

Purpose

To ease out difficulty in studying individually the chemistry of all the elements and their compounds.

Genesis of Periodic Classification

- •Law of Triads: Johann Dobereiner (1829)
- •Law of Octaves: John Alexander Newlands (1865)
- •Periodic Law: Dimitri Mendeleev and Lothar Meyer.
It states that the properties of the elements are periodic function of their atomic weights.
- •Modern Periodic Law: Henry Moseley (1913)
It states that the physical and chemical properties
of the elements are periodic functions of their atomic numbers. ; Horizontal rows –Periods, Vertical columns – Groups –are numbered from 1 to 18.

IUPAC Nomenclature of Elements with Atomic numbers > 100:

Derived from the atomic number of element using numerical roots for 0 and numbers 1-9 and "ium" is added at the end.

Properties of Elements based on Electronic Configuration

- •Electronic Configuration is the distribution of electrons into orbitals of an atom.
- •In periods: Number of elements in each period is twice the number of
atomic orbitals available in the energy level that is being filled.
- •Group wise: Elements in same group have similar valence shell electronic configurations. Same number of electrons in outer orbitals and similar properties. These are classified into four blocks i.e., s-block, p-block, d-block and f-block.

Periodic Table Classification based on Types of Elements

f-Block: Elements

- Also called as Inner Transition Elements.
- Contains Lanthanoids and Actinoids.
- Outer configuration ie $(n-2)\ f^{1-14}\ (n-1)\ d^{1-10} ns^{0-2}$
- All are metals.
- Actinoids are radioactive.

d-Block: Elements

- Group 3-12
- Outer configuration is $(n-1)\ d^{1-10}\ ns^2\ np^6$
- Forms coloured ions.
- Exhibit variable valence, paramagnetism.
- Also called as Transition elements.
- Some are used as catalysts.

p-Block: Elements

- Group 13 to 18.
- Also called as representatives or main group elements.
- Outermost configuration varies from ns^2np^1 to $ns^2\ np^6$
- At the end of period are low reactive noble gases.
- Halogens and Chalcogens have high negative electron gain enthalpies.
- Metallic character increases down the group.

s-Block: Elements

- Group 1 (alkali metals) and Group 2 (alkaline earth metals)
- Outermost configuration is ns^1 or ns^2
- Reactive with low IE.
- Metallic character and reactivity increases down the group.

Important Questions

Multiple Choice questions-

1. The group number, number of valence electrons, and valency of an element with the atomic number 15, respectively, are:
   (a) 16, 5 and 2
   (b) 15, 5 and 3
   (c) 16, 6 and 3
   (d) 15, 6 and 2

2. The d-block elements consist mostly of
   (a) Monovalent metals
   (b) All non-metals
   (c) Elements which generally form stoichiometric metal oxide
   (d) Many metals with catalytic properties

3. Which of the following has the highest boiling point?
   (a) Ne
   (b) Xe
   (c) Ar
   (d) Kr.

4. The chemistry of lithium is very similar to that of magnesium even though they are placed in different groups. Its reason is:
   (a) Both are found together in nature
   (b) Both have nearly the same size
   (c) Both have similar electronic configuration
   (d) The ratio of their charge and size (i.e. charge density) is nearly the same

5. Which one of the following groupings represents a collection of isoelectronic species? (At. nos: Cs-55, Br-35)
   (a) Na^+, Ca^{2+}, Mg^{2+}
   (b) N^{3-}, F–, Na+
   (c) Be, Al^3+, Cl^-
   (d) Ca^{2+}, Cs^+, Br

6. Which of the following has the maximum number of unpaired electrons?
   (a) Mg^{2+}
   (b) Ti^{3+}
   (c) V^{3+}
   (d) Fe^{2+}

7. In the periodic table, the element with atomic number 16 will be placed in the group
   (a) Third
   (b) Fourth
   (c) Fifth
   (d) Sixth

8. Representative elements are those which belong to
   (a) p and d – Block
   (b) s and d – Block
   (c) s and p – Block
   (d) s and f – Block

9. Which pair of elements belongs to same group?
   (a) Elements with atomic no. 17 and 38
   (b) Elements with atomic no. 20 and 40
   (c) Elements with atomic no. 17 and 53
   (d) Elements with atomic no. 11 and 33

10. The most electronegative element of the periodic table is
    (a) Iodine
    (b) Sulphur
    (c) Oxygen
    (d) Fluorine.

11. In the third period of the Periodic Table the element having smallest size is
    (a) Na
    (b) Ar
    (c) Cl
    (d) Si

12. The element with highest second ionization energy is
    (a) Cl
    (b) S
    (c) Na
    (d) Mg

13. Which of the following properties generally decreases along a period?
    (a) Ionization Energy
    (b) Metallic Character
    (c) Electron Affinity
    (d) Valency.

14. Increasing order of electronegativity is
    (a) Bi < P < S < Cl
    (b) P < Bi < S < Cl
    (c) S < Bi < P < Cl
    (d) Cl < S < Bi < P
15. Which of the following oxides is amphoteric in character?
    (a) SnO_2 (b) CO_2
    (c) SiO_2 (d) CaO

Very Short Questions:

1. An element is present in the third period of the p-block. It has 5 electrons in its outermost shell. Predict its group. How many unpaired electrons does it have?
2. An element X with Z = 112 has been recently discovered. Predict its electronic configuration and suggest the group in which it is present.
3. The electronic configuration of an element is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$. Name the period and the group to which it belongs?
4. Arrange Cl, Cl^-, Cl^+ ion in order of increasing size.
5. Arrange the following in increasing order of size.

   N^{3-}, Na^+, F^-, O^{2-}, Mg^{2+}
6. Give the formula of one species positively charged and one negatively charged that will be isoelectronic with Ne.
7. Argon has atomic number 18 and belongs to the 3rd period and 18th group. Predict the group and period for the element having atomic number 19.

Short Questions:

1. Do elements with high I.E. have high E.A.?
2. What is a periodic classification of elements?
3. Distinguish between s and p block elements.
4. Explain why ionization enthalpies decrease down a group of the Periodic Table.
5. Why does the first ionization enthalpy increase as we go from left to right across a given period of the Periodic Table.
6. How do atomic radii vary across a period with an atomic number in the periodic table?

Long Questions:

1. Electronic configuration of the four elements are given below:

   Arrange these elements in increasing order of their metallic character. Give reasons for your answer.
   (i) $[Ar]4^{s2}$
   (ii) (ii) $[Ar]3d^{10}\ 4s^2$
   (iii) $[Ar]3d^{10}\ 4s^2\ 4p^6\ 5s^2$
   (iv) $[Arl\ 3d^{10}\ 4s^2\ 4p^6\ 5s^1$
2. Explain the important general characteristics of groups in the modem periodic table in brief.
3. Explain the electronic configuration in periods in the periodic table. „
4. Explain the variation of valence in the periodic table.

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): Generally, ionisation enthalpy increases from left to right in a period.

   Reason (R): When successive electrons are added to the orbitals in the same principal quantum level, the shielding effect of inner core of electrons does not increase very much to compensate for the increased attraction of the electron to the nucleus.
   (i) Assertion is correct statement and reason is wrong statement.
   (ii) Assertion and reason both are correct statements and reason is correct explanation of assertion.
   (iii) Assertion and reason both are wrong statements.
   (iv) Assertion is wrong statement and reason is correct statement.
2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): Boron has a smaller first ionisation enthalpy than beryllium.

   Reason (R): The penetration of a 2s electron to the nucleus is more than the 2p electron hence

2p electron is more shielded by the inner core of electrons than the 2s electrons.

(i) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(ii) Assertion is correct statement but reason is wrong statement.

(iii) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(iv) Assertion and reason both are wrong statements.

Case Study Based Question:

1. Comprehension given below is followed by some multiple-choice questions. Each question has one correct option. Choose the correct option. In the modern periodic table, elements are arranged in order of increasing atomic numbers which is related to the electronic configuration. Depending upon the type of orbitals receiving the last electron, the elements in the periodic table have been divided into four blocks, viz, s, p, d and f. The modern periodic table consists of 7 periods and 18 groups. Each period begins with the filling of a new energy shell. In accordance with the Arfbau principle, the seven periods (1 to 7) have 2, 8, 8, 18, 18, 32 and 32 elements respectively. The seventh period is still incomplete. To avoid the periodic table being too long, the two series of f-block elements, called lanthanoids and actinoids are placed at the bottom of the main body of the periodic table.

(1) The element with atomic number 57 belongs to

(a) s-block

(b) p-block

(c) d-block

(d) f-block

(2) The last element of the p-block in 6th period is represented by the outermost electronic configuration.

(a) 7s2 7p6

(b) 5f14 6d10 7s2 7p0

(c) 4f14 5d10 6s2 6p6

(d) 4f14 5d10 6s2 6p4

(3) Which of the elements whose atomic numbers are given below, cannot be accommodated in the present set up of the long form of the periodic table?

(a) 107 (b) 118

(c) 126 (d) 102

(4) The electronic configuration of the element which is just above the element with atomic number 43 in the same group is _______.

(a) 1s2 2s2 2p6 3s2 3p6 3d5 4s2

(b) 1s2 2s2 2p6 3s2 3p6 3d5 4s3 4p6

(c) 1s2 2s2 2p6 3s2 3p6 3d6 4s2

(d) 1s2 2s2 2p6 3s2 3p6 3d7 4s2

(5) The elements with atomic numbers 35, 53 and 85 are all _______.

(a) Noble gases

(b) Halogens

(c) Heavy metals

(d) Light metals

2. Read the passage given below and answer the following questions:

When an electron is added to a gaseous atom in its ground state to convert it into a negative ion, the enthalpy change accompanying the process is called the electron gain enthalpy (Δe_g H). It is a direct measure of the ease with which an atom attracts an electron to form anion.

$$X(g)+e^{-} \longrightarrow X^{-}(g); H = e_g H$$

The most stable state of an atom is the ground state. If an isolated gaseous atom is in excited state, comparatively lesser energy will be released on adding an electron. So, electron gain enthalpies of gaseous atoms must be determined in their ground states. Therefore, the terms ground state and isolated gaseous atom has been also included in the definition of electron gain enthalpy. Like ionisation enthalpy, electron gain enthalpy is measure either in electron volts per atom or kJ per mole.

(1) Noble gases have positive electron gain enthalpy due to:

(a) Stable configuration

(b) Large size

(c) High reactivity

(d) Unstable configuration

(2) The electron gain enthalpy of O or F is less than that of S or Cl. It is due to:

(a) Small size

(b) Less repulsion

(c) Large size

(d) High electronegativity

(3) The electron gain enthalpy (in kJ/mol) of fluorine, chlorine, bromine and iodine, respectively, are:

(a) -333, -325, -349 and -296

(b) -296, -325, -333 and -349

(c) -333, -349, -325 and -296

(d) -349, -333, -325 and -296

(4) Why beryllium has higher ionization enthalpy than boron?

(a) More penetration of s-electron

(b) More penetration of p-electron

(c) Large size

(d) Small size

Answer Key

MCQ Answers:

1. (a) 15, 5 and 3
2. (d) Many metals with catalytic properties
3. (b) Xe
4. (d) The ratio of their charge and size (i.e. charge density) is nearly the same
5. (b) N^{3-}, F^{-}, Na+
6. (d) Fe^{2+}
7. (d) Sixth
8. (c) s and p – Block
9. (c) Elements with atomic no. 17 and 53
10. (d) Fluorine.
11. (b) Ar
12. (c) Na
13. (b) Metallic Character
14. (a) Bi < P < S < Cl
15. (a) SnO_2

Very Short Answer:

1. It belongs to the 15th group (P). It has 3 unpaired electrons.
2. Rn] $5f^{14}$ $6d^{10}$ $7s^2$. It belongs to the 12th group.
3. Third-period Group 17.
4. CP < Cl < CP.
5. $Mg^2 + < Na^+ < F^- < O^{2-} < N^{3-}$
6. Na^+, F^-.
7. Group I, Period 4th.

Short Answer:

1. **Ans:** Normally is true that the elements with haying high value of I.E. have a high value of E affinity. But however, there are marked exceptions. It is seen that elements, with stable electronic configurations, have very high values of I-Energies as it is difficult to remove electrons as is the case with 15th and 18th group elements but in such case, electron cannot be added easily so that is why elements of 15th group have almost zero E.A. and elements of 18th group have got zero E.A. whereas their Ionization energy values are very high.
2. **Ans:** By periodic classification of the elements we mean the arrangement of the elements in such a way that the elements with similar physical and chemical properties are grouped together and for this various scientist made contributions but however the contributions made by Mendeleev are of great significance and he gave a periodic table which called as Mendeleev's Periodic 'Table which was older and replaced by the long form of the periodic table.
3. **Ans:** They can be distinguished as follows: s block elements:
    1. They have got the general configuration of the valence shell, ns^{1-2}.
    2. They are all metals.
    3. Their compounds are mostly ionic.
    4. They are generally strong reducing agents.

5. They mostly impart characteristic color to the flame.
6. They have low ionization energies.
7. They show fixed oxidation states.

p block elements:

1. The valence shell electronic configuration of p block elements in $ns^2\ p^{1-6}$.
2. They are mostly non-metals.
3. Their compounds are mostly covalent.
4. They are generally strong oxidizing agents.
5. Mostly they do not impart color to the flame.
6. They have got a comparatively higher value of I.E.
7. They show variable oxidation states.

4. **Ans:** The decrease in ionization enthalpies down any group is because of the following factors:

1. There is an increase in the number of the main energy shells
2. moving from one element to another.
3. There is also an increase in the magnitude of the screening effect due to the gradual increase in the number of inner electrons.

5. **Ans:** The value of ionization enthalpy increases with the increase in atomic number across the period.

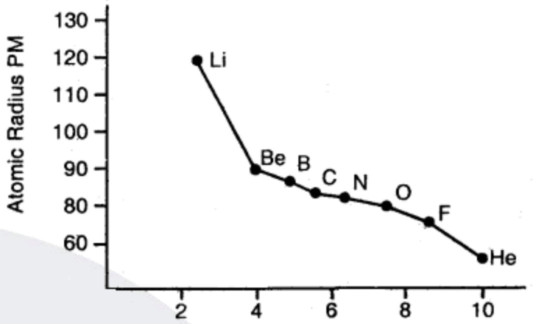
This is due to the fact that in moving across the period from left to right.,

1. Nuclear charge increases regularly by one unit.
2. The progressive addition of electrons occurs at the same level.
3. Atomic size decreases.

This is due to the gradual increase in nuclear charge and a simultaneous decrease in atomic size the electrons are more and more tightly bound to the nucleus. This results in a gradual increase in ionization energy across the period.

6. **Ans:** Variation of Atomic radii across a period: atomic radii decrease with the increase in the atomic number in a period. For example, atomic radii decrease from lithium to fluorine in the second period.

In moving from left to right across the period, the nuclear charge increases progressively by one unit but the additional electron goes" to the same principal shell. As a result, the electron cloud is pulled closer to the nucleus by increased effective nuclear charge. This causes a decrease in atomic size.



Variation of the atomic radius with an atomic number across the second period

Long Answer:

1. **Ans:**

(i) [Ar]4s2 is Calcium metal with At. no. = 20.

(ii) [Ar]$3d^{10}\ 4s^2$ is Zinc metal with At. no. = 30.

(iii) [Ar]$3d^{10}\ 4s^2\ 4p^6\ 5s^2$ is Strontium metal with At. no. = 38.

(iv) [Ar] $3d^{10}\ 4s^2\ 4p^6$, $5s^1$ is*Rubidium metal with At. no. = 37.

Alkali metals are the most metallic, followed by alkaline earth metals and transition metals. Among alkali metals – Rubidium (37) is the most metallic. Among alkaline earth metals (Ca, Sr) Sr (Strontium) is more metallic than Calcium (Ca) as the metallic character increases from top to bottom in a group. Zinc – the transition metal is the least metallic. Thus, metallic character increases from

Zn < Ca < Sr < Rb or (ii) < (i) < (iii) < (iv)

2. **Ans:** The elements of a group show the following important similar characteristics.

(i) **Electronic configuration.** All elements in a particular group have similar outer electronic configuration e.g., all elements of group I', i.e., alkali metals have ns^1 configuration in their valency shell. Similarly, group 2 elements (alkaline Earths) Haye ns^2 outer configuration and halogens (group 17) have $ns^2\ np5$ configuration (where n is the outermost shell).

(ii) **Valency.** The valency of an element depends upon the number of electrons in the outermost shell. So, elements of a group show the same valency, e.g., elements of group 1 show + 1 valency and group 2 show + 2 valencies i.e. valency i.e., NaCl > MgC^{l2} etc.

(iii) **Chemical properties.** The chemical properties of the elements are related to the number of electrons in the outermost shell of their atoms. Hence all elements belonging to the same group show similar chemical properties. But the degree of reactivity varies gradually from top to bottom in a group. For example, in group 1 all the elements are highly reactive metals but the degree of reactivity increases from Li to Cs. Similarly, elements of group 17, i.e., halogens: F, Cl, Br, I are all non-metals and they're- reactivity goes on decreasing from top to bottom.

3. **Ans:** Each successive period in the periodic table is associated with the filling Up of the next higher principal energy level (n – 1, n – 2, etc.). It can be readily seen that the number of elements in each period is twice the number of atomic orbitals available in the energy level that is being filled. The first period starts with the filling of the lowest level (1s) and has thus the two elements – hydrogen ($1s^1$) and helium ($1s^2$) when the first shell (K) is completed. The second period starts with lithium and the third electron enters the 2s orbital.

The next element, beryllium has four electrons and has the electronic configuration $1s^2\ 2s^2$. Starting from the next element boron, the 2p orbitals are filled with electrons when the L shell is completed' at neon ($2s^2\ 2p^6$). Thus there are 8 elements in the second period. The third period (n = 3) being at sodium, and the added electron enters a 3s orbital. Successive filling of 3s and 3p orbitals give rise to the third period of 8 elements from sodium to argon.

The fourth period (n = 4) starts at potassium with the filling up of 4p of 4s orbital. Before the 4p orbital is filled, the filling up of 3d orbitals becomes energetically favorable and we come across the so-called 3d transition series of elements. The fourth period ends at krypton with the filling up of the 4p orbitals. Altogether we have 18 elements in the fourth period. The fifth period (n = 5) beginning with rubidium is similar to the fourth period and contains the 4d transition series starting at yttrium (Z = 39).

This period ends at xenon with the filling up of the 5p orbitals. The sixth period (n = 6) contains 32 elements and successive electrons enter 6s, 4/, 5d, and 6p orbitals, in that order. Filling up of the 4/ orbitals being with cerium, (Z = 58) and ends at lutetium (Z = 71) to give the 4/-inner transition series which is called the lanthanide series. The seventh period (n = 7) is similar to the sixth period with the successive filling up of the 7s, 5f, 6d, and 7p orbitals and includes most of the man-made radioactive elements.

This period will end at the element with atomic number 118 which would belong to the noble gas family. Filling up of the 5f orbitals after actinium (Z = 89) gives the 5f-inner transition series known as the actinide series. The 4f and 5f transition series of elements are placed separately in the periodic table to maintain its structure and to preserve the principle of classification by keeping elements with similar properties in a single column.

4. **Ans:** Variation of valence in a group as well as across a period in the periodic table occurs as follows:

1. **In a group:** All elements in a group show the same valency. For example, all alkali metals (group 1) show a valency of 1+. Alkaline earth metals (group 2) show a valency of 2+.

   However, the heavier elements of p-block elements (except noble gases) show two valences: one equal to the number of valence electrons or 8-No. of valence electron# and the other two less. For example, thallium (Tl) belongs to group 13. It shows valence of 3+ and 1+.

Lead (Pb) belongs to group 14. If shows valance of 4+ and 2+.

Antimony (Sb) and Bismuth (Bi) belong to group 15. They show valence of 5+ and 3+ being more stable.

This happens due to the non-participation of tie two s-electrons present in the valence shell of these elements. This non-participation of one pair of s-electrons in bonding is called the inert-pair effect.

2. **In a period:** The number of the valence electrons increases – in going from left to right in a period of the periodic table. Therefore, the valency of the elements in a period first increase, and then decreases.

Assertion Reason Answer:

1. (ii) Assertion and reason both are correct statements and reason is correct.
2. (iii) Assertion and reason both are correct statements and reason is correct.

Case Study Answer:

1. **Answer:**

   (1) (c) d-block

   (2) (c) 4f14 5d10 6s2 6p6

   (3) (c) 126

   (4) (a) 1s2 2s2 2p6 3s2 3p6 3d5 4s2

   (5) (b) Halogens

2. **Answer:**

   (1) (a) Stable configuration

   (2) (a) Small size

   (3) (c) -333, -349, -325 and -296

   (4) (a) More penetration of s-electron

◆◆

Chemical Bonding and Molecular Structure

4

Introduction

Structure and Bonding is the heart of chemistry. Chemical bond is very important to explain the properties and structure of compound. The important aspect of each type of force is its relative strength, how rapidly it decreases with increasing distance and whether it is directional in nature or not.

Chemical Bond

It is the force of attraction between two atoms which hold them together in a compound or molecule. Nature loves stability and bond formation is associated with stability. Every element has a tendency to occupy inert electronic configuration which is considered as very stable. Noble gas electronic configuration can be achieved by

1. Transference of electrons
2. Mutual sharing of electrons
3. Donation of lone pair of electrons

Types of Bonds:

In order to explain the formation of a chemical bond in terms of electrons, Lewis postulated that atoms achieve stable octet when they are linked by a chemical bond. On the basis of this chemical bonds are following type:

1. Ionic bond
2. Covalent bond
3. Co-ordinate bond
4. Metallic bond
5. Hydrogen bond
6. van der Waal's bond

Lewis Dot Structures

Valence Electrons: In the formation of a molecule only the outer shell electrons take part in chemical bond combination and they are known as valence electrons. In Lewis symbols, an element is shown with symbol and valence electrons.

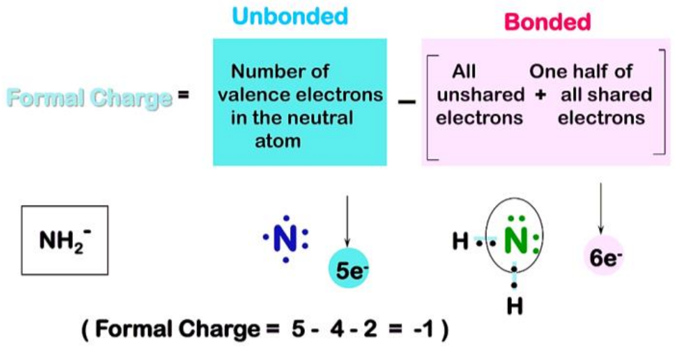
Octet Rule

It is proposed by Kossel and Lewis and according to this, "Every atom has a tendency to attain Noble gas electronic configuration or to have 8 valence electrons". This is known as law of octet rule or if it has two valence electrons then this is known as law of duplet. According to Lewis, only those compounds will be stable which follow octet rule.

Formal Charge

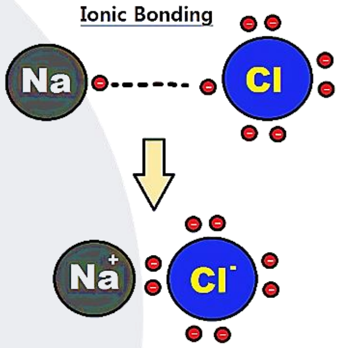
Formal charge on an atom is the difference between the number of valence electrons is an isolated atom and the number of electrons assigned to that atom in a Lewis structure. It is expressed as:

FORMAL CHARGE



Ionic Bond

An ionic bond is formed by complete transference of one or more electrons from the valence shell of one atom to the valence shell of another atom. In this way both the atoms acquire stable electronic configurations of noble gases. The atom which loses electron becomes a positive ion and the atom which gains electron becomes negative ion.



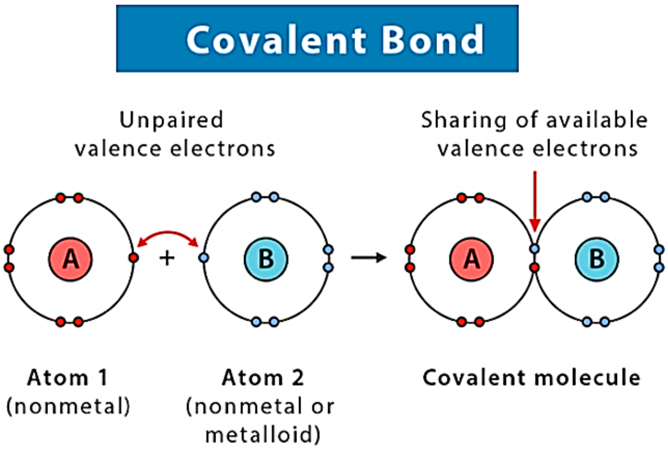
Note: Electro valency is the number of electrons lost or gained during the formation of an ionic bond or electrovalent bond.

Characteristics of Ionic Compounds:

1. They are hard, brittle and crystalline.
2. They have high melting and boiling points.
3. They are polar in nature.
4. The linkage between oppositely charged ions is non rigid and non-directional.
5. They are soluble in polar solvents such as water and insoluble in non-polar solvents such as CCl_4, Benzene, ether etc.
6. They are good conductors of electricity in fused state and in solution due to mobility of the ions. They are bad conductors of electricity in solid state because ions are unable to move.

Covalent Bond

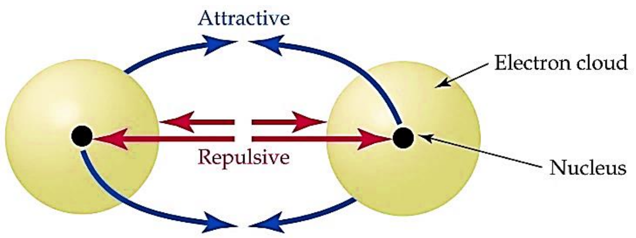
A force which binds atoms of same or different elements by mutual sharing of electrons is called a covalent bond. If the combining atoms are same the covalent molecule is known as homoatomic. If they are different, they are known as heteroatomic molecule.



Valence Bond Theory (VBT)

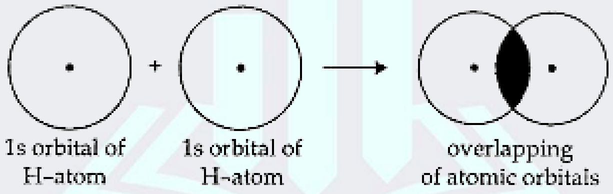
Valence bond theory was introduced by Heitler and London (1927) and developed by Pauling and others. It is based on the concept of atomic orbitals and the electronic configuration of the atoms. Let two hydrogen atoms A and B having their nuclei NA and NB and electrons present in them are eA and eB. As these two atoms come closer new attractive and repulsive forces begin to operate.

1. The nucleus of one atom is attracted towards its own electron and the electron of the other and vice versa.
2. Repulsive forces arise between the electrons of two atoms and nuclei of two atoms. Attractive forces tend to bring the two atoms closer whereas repulsive forces tend to push them apart.



Orbital overlap concept

If we refer to the minimum energy state in the formation of hydrogen molecule the two H-atoms are enough near so as to allow their atomic orbitals to undergo partial interpenetration. This partial interpenetration of atomic orbitals is called overlapping of atomic orbitals. The overlap between the atomic orbitals can be positive, negative or zero depending upon the characteristics of the orbitals participating to overlap.

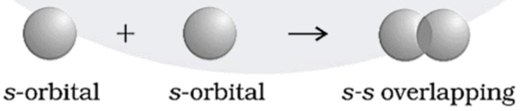


Types of overlapping

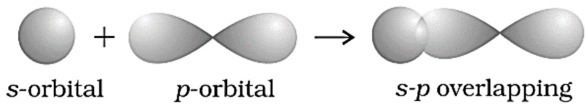
The covalent bonds can be classified into two different categories depending upon the type of overlapping. These are:

Sigma (σ) bond: This type of covalent bond is formed by the axial overlapping of half-filled atomic orbitals. The atomic orbitals overlap along the internuclear axis and involve end to end or head on overlap. There can be three types of axial overlap among s and p-orbitals as discussed below:

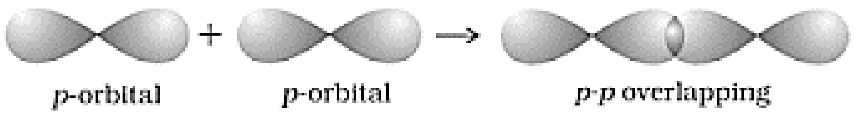
i. **s-s overlap:** In this case, there is overlap of two half-filled s-orbitals along the internuclear axis as shown below.



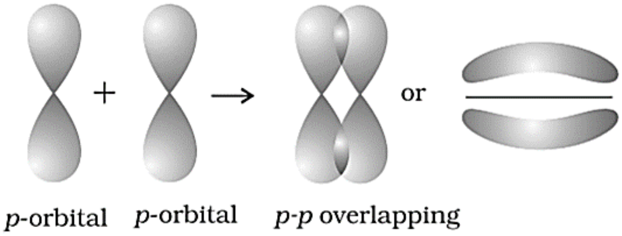
ii. **s-p overlapping:** It involves the overlapping of half-filled s-orbitals of one atom with the half-filled p-orbitals of the other atom. The bond thus formed is called s-p sigma bond.



iii. **p-p overlapping:** It involves the co-axial overlapping between half-filled p-orbitals of one atom with half-filled p-orbitals of the other atom. The bond as formed is called p-p sigma bond.



pi (π) bond: This type of covalent bond is formed when the atomic orbitals overlap in such a way that their axis remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms. The electrons involved in the π bond formation are called pi-electrons.



Hybridisation: Hybridisation is the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape. The atomic orbitals combine to form new set of equivalent orbitals known as hybrid orbitals.

Salient Features of Hybridisation:

i. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.

ii. The hybridised orbitals are always equivalent in energy and shape.

iii. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.

iv. The type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation:

i. The orbitals present in the valence shell of the atom are hybridised.

ii. The orbitals taking part in hybridisation must have only a small difference of energies.

iii. Promotion of electron is not essential condition prior to hybridisation.

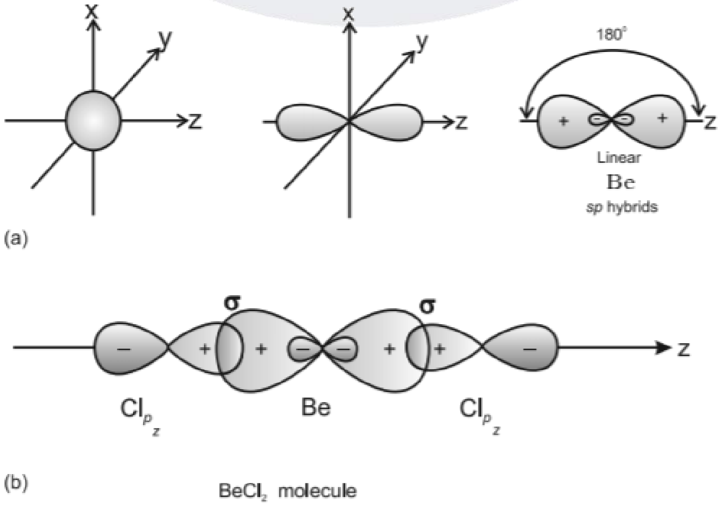
iv. It is not necessary that only half-filled orbitals participate in hybridisation.

Types of hybridisation

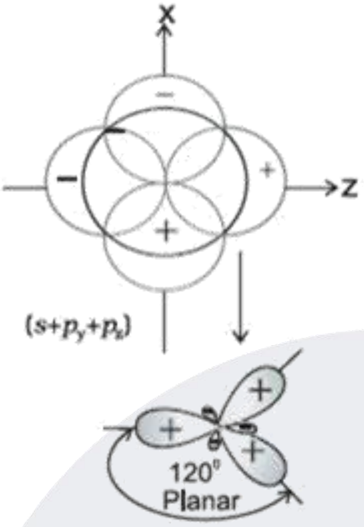
There are many different types of hybridisation depending upon the type of orbitals involved in mixing such as sp^3, sp^2, sp, sp^3d, sp^3d^2 etc.

i. **sp-hybridisation:** In this hybridisation one s and one p orbitals hybridise to produce two equivalent hybrid orbitals, known as sp hybrid orbitals. The two sp-hybrid orbitals are oriented in a straight line making an angle of 180° and therefore the molecule possesses linear geometry. Each of hybrid orbitals has 50% s-character and 50% p-character.

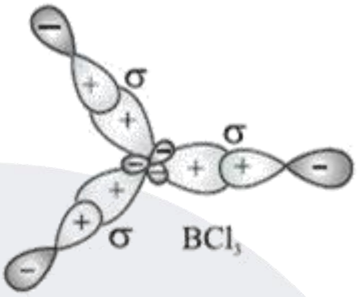
Example of molecules having sp-hybridisation are BeF_2, $BeCl_2$, BeH_2 etc.



ii. **sp^2-hybridisation:** In this hybridisation one s and one 2p orbitals hybridise to produce three equivalent hybrid orbitals, known as sp^2 hybrid orbitals. sp^2 hybrid orbitals are larger in size than sp-hybrid orbitals but slightly smaller than that of sp^3 hybrid orbitals. Each sp^2 hybrid orbitals has 1/3 (or 33.33%) s-character and 2/3 (or 66.7%) p-character. Example, BF_3, BCl_3, BH_3 etc.

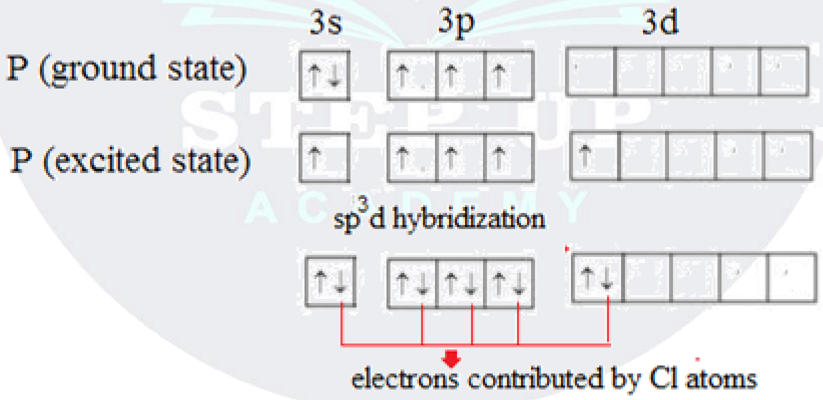


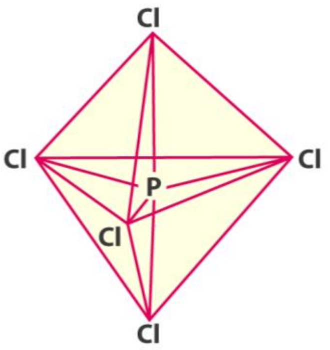
sp^2 hybrids



iii. **sp^3d-hybridisation:** This type of hybridisation involves mixing of ones, three p and one d-orbitals to form five sp^3d hybridised orbitals which adopt trigonal bipyramidal.

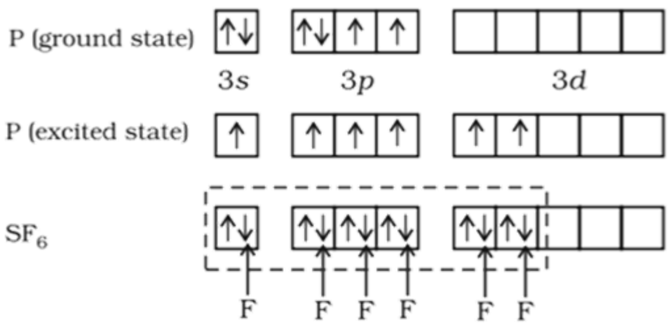
Formation of PCl_5: The ground state electronic configuration of phosphorus is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$. Under the conditions of bond formation, the 3s-electrons get unpaired and one of the electrons is promoted to vacant $3dz^2$ orbital. The ground state and excited state configurations of phosphorus are shown below:



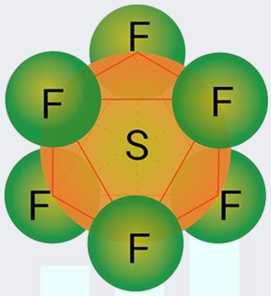


iv. **sp^3d^2-hybridisation:** In this type of hybridisation ones, three p and two d-orbitals undergo intermixing to form six identical sp^3d^2 hybrid orbitals. These six orbitals are directed towards the corners of an octahedron and lie in space at an angle of 90° to one another.

The ground state outer configuration of 16S is $3s^2$ $3p^4$. In the excited state the electron pairs in 3s and 3px orbitals get unpaired and one out of each pair is promoted to vacant $3dz^2$ and $3dx^2$-y^2 orbitals. The ground state and excited state configuration of 16S are given as follows:



sp^3d^2 hybridisation



Valence Shell Electron Pair Repulsion (VSEPR) Theory

Sidgwick and Powell in 1940, proposed a simple theory based on repulsive character of electron pairs in the valence shell of the atoms. It was further developed by Nyholm and Gillespie (1957). Main Postulates are the following:

i. The exact shape of molecule depends upon the number of electron pairs (bonded or non-bonded) around the central atoms.

ii. The electron pairs have a tendency to repel each other since they exist around the central atom and the electron clouds are negatively charged.

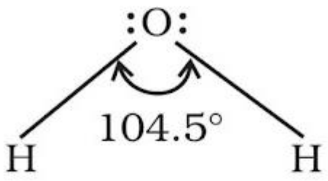
iii. Electron pairs try to take such position which can minimize the rupulsion between them.

iv. The valence shell is taken as a sphere with the electron pairs placed at maximum distance.

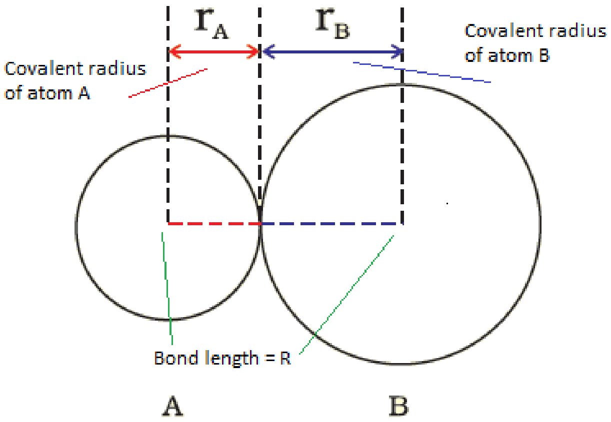
v. A multiple bond is treated as if it is a single electron pair and the electron pairs which constitute the bond as single pairs.

Bond Parameters:

i. **Bond Angle:** It is the distance between two consecutive crests or troughs and is denoted by λ. It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion. Bond angle is expressed in degree which can be experimentally determined by spectroscopic methods.



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



iii. **Lattice Enthalpy:** The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. For example, the lattice enthalpy of NaCl is 788 kJ mol^{-1}.

iv. **Bond Order:** Bond order is defined as half of the difference between the number of electrons present in bonding and antibonding molecular orbitals. The bond order may be a whole number, a fraction or even zero. It may also be positive or negative.

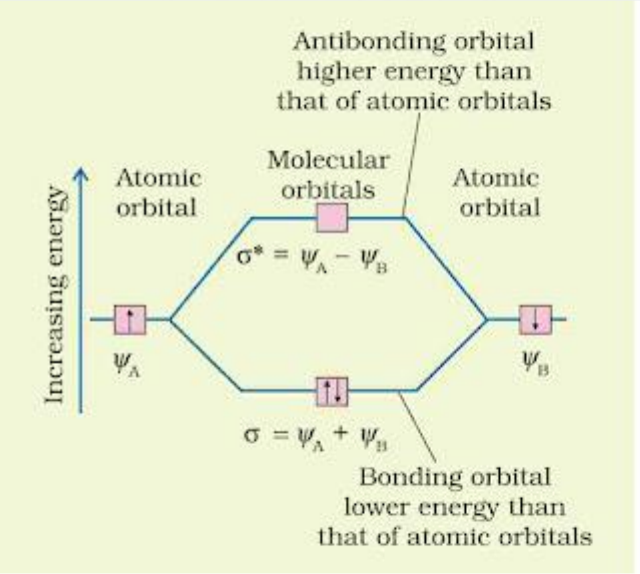
$$\text{Bond order (B.O.)} = \frac{1}{2}[\mathbf{Nb} - \mathbf{Na}]$$

v. **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. For example, the H – H bond enthalpy in hydrogen molecule is 435.8 kJ $mol^{-1.}$

Molecular Orbital Theory (MOT)

Molecular orbital (MO) theory was developed by F. Hund and R.S. Mulliken in 1932. According to MOT, a molecule is considered to be quite different from the constituent atoms. All the electrons belonging to the atoms constituting a molecule are considered to be moving along the entire molecule under the influence of all the nuclei. Thus, a molecule is supposed to have orbitals of varying energy levels, in same way as an atom. These orbitals are called molecular orbitals.

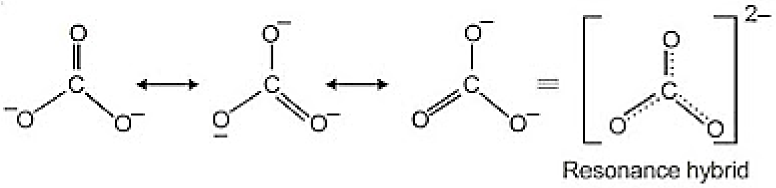
Energy Level Diagram for Molecular Orbitals:



Resonance

When light of a suitable frequency is allowed to incident on a metal, ejection of electrons take place. This phenomenon is known as photo electric effect.

When a compound has same molecular formula but different structural formulas and structures differ with respect to electrons only. These structures are known as resonating structures or canonical structures. None of these structures can explain all the properties of that compound. This phenomenon is known as resonance.



Hydrogen Bonding

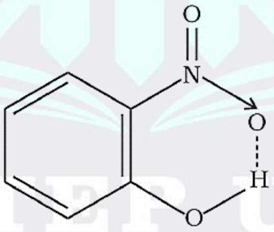
When highly electronegative elements like nitrogen, oxygen, flourine are attached to hydrogen to form covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom. Thus, partial positive charge develops on hydrogen atom which forms a bond with the other electronegative atom. This bond is known as hydrogen bond and it is weaker than the covalent bond.

Types of Hydrogen Bonding:

i. **There are two types of hydrogen bonding:** It is a type of hydrogen bonding between two similar or dissimilar molecules. Example: H – F, HF and water, NH_3, NH_3 and water, alcohol, alcohol and water etc.

$$H^{\delta+} - X^{\delta-} - - - H^{\delta+} - X^{\delta-} - - - H^{\delta+} - X^{\delta-}$$

ii. **Intramolecular hydrogen bonding:** It is a type of hydrogen bonding within the molecule. Example: Salicylaldehyde, O-nitrophenol etc.



Applications of Hydrogen Bonding

i. **State:** Hydrogen bonding may affect the state of a compound. For example, H_2O is liquid at room temperature whereas H_2S is gas. It is due to presence of intermolecular hydrogen bonding between H_2O molecules, which is not present in H_2S molecules.

ii. **Solubility:** Only those covalent molecules are soluble in water which have tendency to form intermolecular hydrogen bonding with water molecules.

iii. **Boiling point:** Intermolecular hydrogen bonding increases the boiling point of compound. For example, NH_3 has higher boiling point than PH_3. This is because, there is intermolecular hydrogen bonding in NH_3 but not in PH_3.

iv. **Density of ice is lower than water:** In ice, hydrogen bonding gives rise to a cage like structure of H–O–H molecules, in which each H–O–H molecule is linked tetrahedrally to four other H–O–H molecule. In this structure, some vacant spaces are formed, which decrease the density of ice.

Metallic Bonding

The force that binds a metal atom to a number of electrons within its sphere of influence is known as metallic bond.

This model could easily explain the following properties of metals:

i. High electrical conductivity

ii. High thermal conductivity

iii. Bright metallic lustre

iv. Malleability

v. Ductility

vi. Tensile strength

vii. Elasticity

Bond Characteristics

Bond Length

When atoms come closer to each other, attraction takes place between them and, therefore, the potential energy of the system keeps on decreasing till at a particular distance, the potential energy is minimum.

If the atoms are further brought closer, the repulsion start and therefore, the potential energy of the system begins to increase.

At equilibrium distance the atoms keep on vibrating about their mean position.

The equilibrium distance between the centres of the nuclei of the two bonded atoms is called its Bond length

It is expressed in terms of angstrom or picometer.

It is determined experimentally by x-ray diffraction or electron diffraction method or spectroscopic method.

In an ionic compound, the bond length is the sum of their ionic radii and in covalent compound, it is the sum of their covalent radii.

For a covalent molecule AB, the bond length is given by d= ra + rb

Factors affecting Bond length

1) **Size of the atoms**

The bond length increases with increase in size of the atom.

HI > HBr > HCl > HF

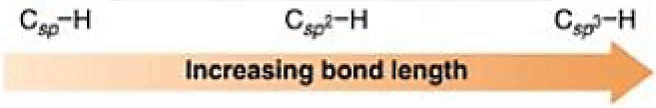
2) **Multiplicity of Bond**

The bond length decreases with the multiplicity of the bond.

$C-C > C=C > C\equiv C$

3) **Type of hybridisation**

An s orbital is smaller in size, greater the s character, shorter is the hybrid orbitals and hence shorter is the bond length.



Bond enthalpy

When atoms come close together resulting in the formation of bond between them, energy is released.

The amount of energy required to break one mole of bonds of a particular type so as to separate them into gaseous atoms is called bond dissociation enthalpy or Bond enthalpy.

Bond enthalpy is usually expressed in KJ mol-1

Greater is the bond dissociation enthalpy, stronger is bond.

For diatomic molecules like H_2 , Cl_2, O_2, N_2, HCl, HBr, HI the bond enthalpies are equal to their dissociation enthalpy and hence have fixed. In case of polyatomic molecules, since a particular type of bond present in different molecules or even in the same molecule do not possess the same bond enthalpy, therefore, bond enthalpy are usually the average values.

In H_2O, first O-H bond enthalpy=502 Kj/mol

Second bond enthalpy= 427 KJ/mol

Average bond enthalpy = (502 + 427) / 2 = 464.5 KJ/mol

Factors affecting bond enthalpy

1) **Size of the atom**

   Greater the size of the atom, greater is the bond length and less is the bond dissociation enthalpy i.e., less is the bond strength.

2) **Multiplicity of bonds**

   Greater is the multiplicity of the bond, greater is the bond dissociation enthalpy.

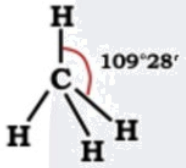
3) **Number of lone pair of electrons present**

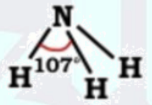
   Greater the number of lone pair of electrons present on the bonded atom, greater is the repulsion between the atoms and hence less is the bond dissociation enthalpy.

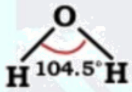
4) **Bond angle**

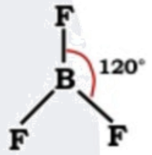
   A bond is formed by the overlap of atomic orbitals. The direction of overlap gives the direction of the bond.

   The angle between the lines representing the direction of the bond i.e. the orbitals containing the bonding electrons is called the bond angle.









5) **Bond order**

   In lewis representation of a molecular or ion, the number of bonds present between two atoms is called the bond order

   For odd electron molecule, as the 3-electron bond is considered as equivalent to half covalent bond, the bond order can be fractional also.

   Greater the bond order, greater is the stability of the bond i.e., greater is the bond enthalpy.

   Greater the bond order, shorter is the bond length.

Polar and Non-Polar Covalent Bond

Non-polar covalent bonds

If two similar atoms come close to each other and form a bond by sharing their electrons, the shared electrons are equally attracted by the two atoms as the electronegativity of the atoms is same.

Hence no poles are developed. This leads to the formation of completely non-polar bonds.

If two hydrogen atoms form a bond, the electron pair will lie exactly in the middle between the two atoms.

The electron cloud is completely symmetrical and there is no charge separation at all.

For Ex: Cl_2 , O_2 , N_2 , F_2

Polar covalent bonds

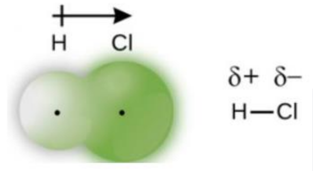
When two dissimilar atoms, having different electro negativities combined together to form a covalent bond, the shared pair of electrons does not lie at equal distance from the nuclei of both the bonded atom but shift towards the atom having greater electronegativity.

The more electronegative atom attracts the electrons more strongly, the distribution of electrons gets distorted i.e. the electron cloud is displaced more towards the more electronegative atom.

One end of the molecule, having more electronegative atom becomes slightly negatively charged while the other end acquires slightly positive charge.

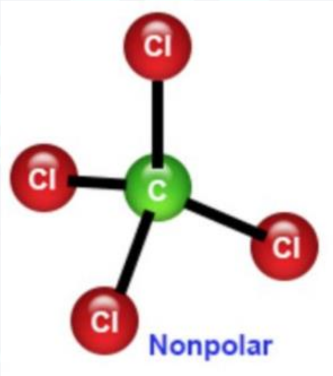
Positive and negative poles are developed and this type of bond is called polar covalent bond.

For Ex: HCl molecule



Chlorine is more electronegative than hydrogen. So the force of attraction, on the shared pair, exerted by chlorine is more than that by the hydrogen. Chlorine becomes slightly negatively charged and hydrogen become slightly positively charged.

In symmetrical molecules like CO_2, CCl_4 , although there are a number of polar bonds present, yet a molecule on the whole or non-polar. This is because the polar bonds cancel the effect of each other.



Partial ionic character of covalent bonds

If two atoms linked together have different electro negativities, the bond formed is polar.

The bond is said to possess partial ionic character.

The extent of partial ionic character is determined by the difference in electronegativity of the combining atoms. More is the difference in electronegativity, greater will be the ionic character.

1) If electronegativity difference between two atoms is 1.9, the bond is said to have 50% ionic character and 50% covalent character.
2) If the electronegativity difference between the two atoms is more than 1.9, the partial ionic character of the bond is more than 50% and the bond is taken as ionic.
3) If the electronegativity difference between two atoms is less than 1.9, the bond is predominantly covalent.

Dipole Moments

In a polar molecule, there are two poles present in the molecule. Hence, the molecule is said to possess an electric dipole. Since the molecule as a whole is electrically neutral, the negative charges is always equal in magnitude to the positive charge.

The product of magnitude of negative or positive charge(q) and the distance between the centres of the positive and negative charges is called dipole moment.

It is usually donated by μ.

It can be expressed as $\mu = q \times d$

The charge q is of the order of 10^{-10} esu and the internuclear distance d is of the order of 10-8 cm.

Therefore, the dipole moment is of order 10^{-18} esu cm.

In S.I. units, $1 \text{ D} = 3.335 \times 10^{-30}$ Cm

Dipole moment and molecular structure

Diatomic molecules

Dipole moment is a vector quantity i.e., it has magnitude as well as direction.

As a polar diatomic molecule possesses only one polar bond, the dipole moment of that molecule is equal to the dipole moment of the polar Bond.

In HCl, the molecular dipole moment is equal to the dipole moment of H-Cl bond i.e 1.07 D.

Greater the electronegativity difference between the bonded atom, greater if the dipole moment. Dipole moment of hydrogen halides are in the order:

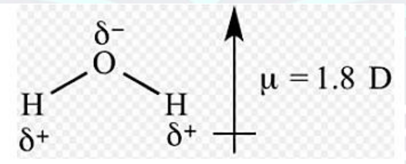
H-F > H-Cl > H-Br > H-I

Polyatomic molecules

As a polyatomic molecule has more than one polar bond, the dipole moment is equal to the resultant dipole moment of all the individual bonds.

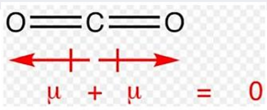
The magnitude of resultant dipole moment not only depends upon the values of the individual dipole moment of the bonds but also on their arrangement in space.

Dipole moment of water is 1.84 D which is equal to the resultant dipole moment of two O-H bonds.

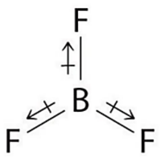


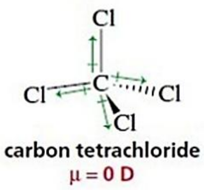
In case of ammonia, the dipole moment of molecule i.e., 1.47 D is the resultant of the dipole moment of the individual dipole moments of N-H bonds.

In carbon dioxide molecule, there are two polar bonds. These polar bonds possess the same value of dipole moment but the overall dipole moment of molecule is found to be zero. Individual dipole moment in this molecule is of equal magnitude but their directions are opposite to each and hence cancel out.



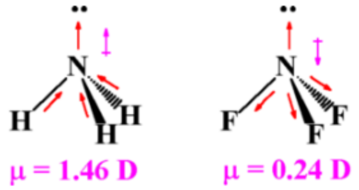
In symmetrical molecules like Boron trifluoride (BF_3) Methane (CH_4) and carbon tetrachloride (CCl_4), the molecular dipole moment is found to be zero. Individual dipole moments cancel out on account of the symmetry of the molecule. In BF_3, the resultant of two bond moments being equal and opposite to that of the third cancel out.





$CHCl_3$ is also tetrahedral but has a dipole moment of 1.04.

Dipole moment of NH_3 and NF_3



Both NH_3 and NF_3 molecules have pyramidal shape with one lone pair of electrons on N atom. As fluorine is highly electronegative, it appears that N-F bond should be more polar and the net dipole moment of NF_3 should be much greater than that of NH_3.

The dipole formed between the lone pair and nitrogen atom has to be taken into consideration which is in the direction of the lone pair.

F is more electronegative than nitrogen, therefore direction of bond is from nitrogen to fluorine whereas nitrogen is more electronegative than hydrogen, the direction of bond is from hydrogen to nitrogen.

Resultant moment of N-H bond adds up to the bone moment of the lone pair, that of 3 N-F bonds partly cancel the resultant of the lone pair. Hence the net dipole moment of NF_3 is less than that of NH_3.

Application of dipole moment

1) In determining the polarity of bonds:

   Greater is the magnitude of dipole moment, higher will be the polarity of the bond. This is applicable to molecules containing only one polar bond. In case of non-polar molecules like H_2 , O_2, N_2 etc. the dipole moment is found to be zero .This is because there is no charge separation in these molecules.

2) In determining the symmetry of the molecules

   If any molecule possesses two or more polar bonds, it will not be symmetrical if it possesses some molecular dipole moment.

   Water μ = 1.84 D

   H_2S μ = 0.95 D

   NH_3 μ = 1.47 D

   If a molecule contains a number of similar atoms linked to the central atom and the overall dipole moment of the molecule is found to be zero, this will imply that the molecule is symmetrical.

   For Ex: BF_3 , CH_4 , CCl_4

3) To distinguish between cis and trans isomers

   Cis isomer usually has higher dipole moment than trans isomer.

4) To distinguish between Ortho, meta and para isomers

   The dipole moment of para isomer is zero and that of ortho is greater than that of meta.

Fajan’s Rules

When a cation approaches an anion, the electron cloud of the anion is attracted towards a cation and hence gets distorted. The effect is called polarisation of the anion.

The power of cation to polarise anion is called its polarising power and tendency of the anion to get polarised is called polarisability. The greater is the polarisation produced, more is the neutralisation of the charges and hence the ionic character decreases or the covalent character increases.

The polarising power of the cation and the polarisability of the anion and hence the formation of covalent bond depends on:

1) Small size of the cation

   Smaller the cation, greater is its polarising power.

2) Large size of the anion

   larger the anion, greater is its polarisability. Covalent character of lithium halides is in the order:

   $$LiI > LiBr > LiCl > LiF$$

3) Large charge on the cation or anion

   Larger the charge on the cation, greater is its polarising power. Hence covalent character increases.

   The covalent character of the chlorides is in the order:

   $$NaCl < MgCl_2 < AlCl_3$$

   Greater the charge on the anion, more easily it gets polarised.

4) Electronic configuration of the cations

   If two cations have the same size and charge, then the one with 18 electrons in the outermost shell has greater polarising power than the other with 8 electrons in the outermost shell.

Characteristics of covalent compounds

1) Physical States: The covalent compounds exist in all the three states i.e., solid, liquid and gases.
2) Crystal structure: The crystal structure of covalent compounds differs from that of ionic compounds. They usually consist of molecules rather than ions.
3) Melting and boiling point: Covalent compounds have low melting and boiling point because the molecules in covalent compounds are held together less rigidly.
4) Solubility: They are generally soluble in organic solvents but insoluble in water and other polar solvents.
5) Electrical conductivity: Since there are no free ions in covalent compounds to conduct electricity, they are bad conductors of electricity.
6) Non-ionic reactions: These compounds are molecular in nature and not ionic, their reactions are molecular and proceed at a much slower rate than those of ionic compounds.
7) Directional characteristics and isomerism: As the atoms in covalent compounds are held together by the shared electrons, it is rigid and directional. Hence, atoms in a molecule can take up different directional arrangement and thus show structural and stereoisomerism.

Shapes Of Molecules

Shape of beryllium fluoride (BeF_2) molecule

Atomic number of Be = 4

Electronic configuration in ground state is $1s^2\ 2s^2$

Electronic configuration in excited state is $1s^2\ 2s^1\ 2p_x^1$

one 2s orbital and one 2p orbital undergo sp hybridisation to form two half-filled sp hybrid orbitals which are oriented at an angle of 180°.

They overlap with the half-filled orbitals of the two fluorine atoms to give a linear shape.

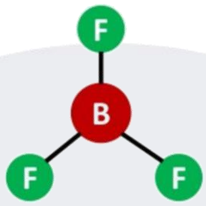
Shape of Boron trifluoride (BF_3) molecule

Atomic number of Boron=5

Electronic configuration in ground state $1s^2\ 2s^2\ 2p_x{}^1$

Electronic configuration in excited state = $1s^2\ \ 2s^1\ 2p_x{}^1$

One 2s and two 2p orbitals undergo sp^2 hybridisation to form 3 half-filled hybrid orbitals which are planar and oriented at an angle of 120° to each other. These overlap with half-filled orbitals of 3 fluorine atoms to form BF^3 which has triangular planar shapes.



Shape of Methane (CH_4) molecule

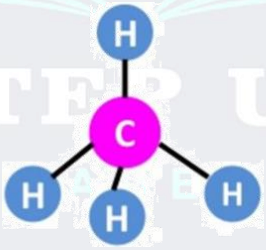
Atomic number of carbon = 6

Electronic configuration in the ground state is $1s^2\ 2s^2\ 2p_x{}^1\ 2p_y{}^1$

Electronic configuration in the excited state is $1s^2\ 2s^1\ 2p_x{}^1\ 2p_y{}^1\ 2p_z{}^1$

One 2s and three 2p orbitals undergo sp^3 hybridisation to form four sp^3 hybrid orbitals which are arranged tetrahedrally at an angle of 109°28´to each other.

The 4 sp^3 hybrid orbitals overlap with the half-filled 1s orbital of 4 hydrogen atoms, forming CH_4.

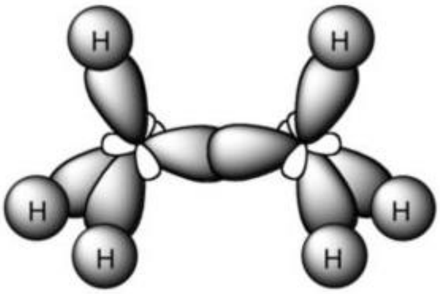


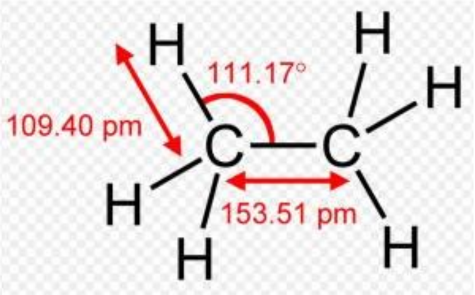
Shape of Ethane molecule(C_2H_6)

In the formation of ethane molecule, each carbon atom undergoes sp^3 hybridisation, thus forming four sp^3 hybrid orbitals directed towards the corners of a tetrahedron and inclined to each other at an angle of 109°28.

One sp^3 hybrid orbital of the first carbon atom undergoes overlapping with one sp^3 hybrid orbitals of second carbon atom along the internuclear axis, thus forming a sigma bond between them.

The remaining 3 sp^3 hybrid orbitals of each carbon atom undergo overlapping with the half-filled 1s orbital of hydrogen atom, each along internuclear axis and hence forming sigma bond.





Shape of ethylene molecule (C_2H_4)

The electronic configuration of carbon atom in the excited state is $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$

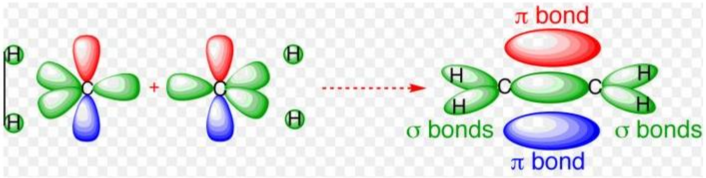
Each carbon atom undergoes sp^2 hybridisation, thus leaving one $2p_z$ orbital is the unhybridized state.

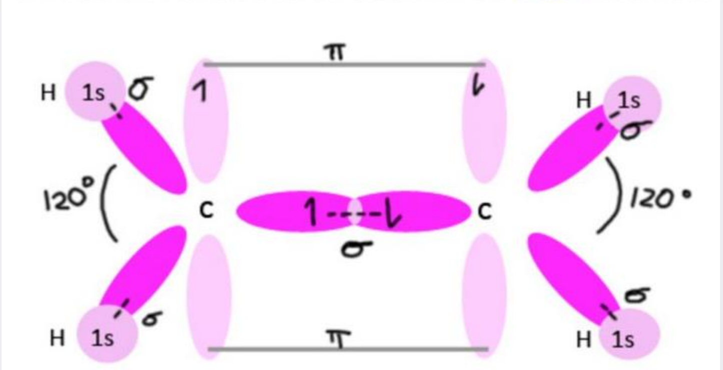
The 3 sp^2 hybrid orbitals of each carbon atom are planar and are inclined to each other at an angle of 120°.

One sp^2 hybrid orbital of the the first carbon atom overlaps with one sp^2 hybrid orbital of the second carbon atom along the internuclear axis thereby forming one sigma bond between them.

The other two sp^2 hybrid orbitals of each carbon atom overlap with the half-filled 1s orbital of hydrogen atom along their respective internuclear axis forming sigma bond.

The unhybridized $2p_z$ orbital of the first carbon atom undergoes sideways overlapping with the unhybridized $2p_z$ orbitals of the second carbon atom, thereby forming a π bond between the two carbon atoms. The two carbon atoms are linked to each other by 1 sigma bond and 1 π bond and each carbon atom is further linked to two hydrogen atoms by sigma bond. The molecule is planar.





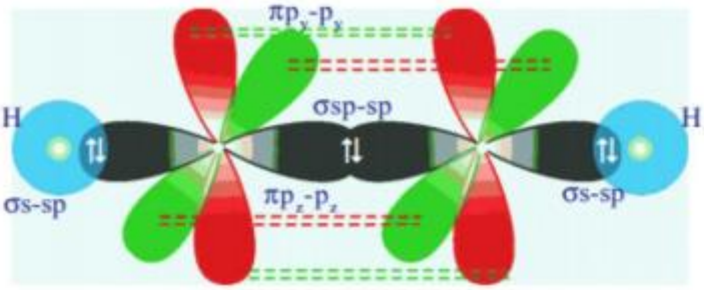
Shape of acetylene molecule

In the formation of acetylene molecule, each carbon atom undergoes sp hybridization leaving two 2p orbitals in the original unhybridised state. The two sp hybrid orbitals of each carbon atom are linear i.e., they are 180° degree apart.

One sp hybrid of the first carbon atom overlaps with one sp hybrid orbital of the second carbon atom along the internuclear axis thus forming sigma bond between them. The second sp hybrid orbital of each carbon atom overlaps with half-filled 1s orbital of hydrogen atom again along the internuclear axis and thus forming Sigma bonds.

The unhybridised $2p_y$ orbital of the first carbon atom undergoes sideways overlapping with the $2p_y$ orbital of the second carbon atom, thereby forming a π bond between the two carbon atoms.

All the carbon and hydrogen atoms are linear and there is electron cloud above and below, in the front and at the back of the C-C axis.



Summary

1. **Chemical Bond:** The force of attraction which holds various chemical entities in different species.
2. Electrovalent Bond: The attractive force between the oppositely charged ions which comes into existence by the transference of electrons.
3. **Electrovalence:** The number of electrons which an atom loses or gains while forming ionic or electrovalent bond.
4. **Covalent Bond:** The bond comes into existence by the mutual sharing of electrons by the atoms participating in bonding.
5. **Valence Bond Approach of Covalent Bond:** The bond is formed by the overlapping of halffilled atomic orbitals having electrons with opposite spins.
6. **Covalency:** The number of half-filled atomic orbitals which an atom provides for participation in overlapping at the time of bonding.
7. **Dative Bond or Co-ordinate Bond:** The bond is formed by sharing of electrons in which the shared pair of electrons is contributed by one of the atom called donor while the other atom is called acceptor.
8. **Hybridisation:** The process of mixing or merging of orbitals (of slightly different energies) of an atom to form another set of orbitals with equivalent shape and energy.
9. **Geometry of the Molecule:** The definite relative arrangement of the bonded atoms in a molecule.
10. **Regular and Irregular Geometry:** The molecule is said to possess regular geometry if the repulsive interactions among the electron pair around the central atom are of equal magnitude. If the repulsive interactions among the electron pairs are unequal, the geometry is referred to as irregular.
11. **Electronegativity:** The power of an atom to attract bonding pair of electrons towards itself.
12. **Dipole Moment (μ):** A vector quantity defined by the product of charge developed on any of the atom and distance between the atoms; creating a dipole.
13. **Polar and Non-Polar Molecules:** The molecules with dipole moment $(\mu) > 0$ are called polar molecules while those with $\mu = 0$ are non-polar molecules.
14. **Dipole-Dipole Interactions:** The attractive interactions among the opposite ends of polar molecules in liquid and solid state.
15. **Hydrogen Bond:** The electrostatic force of attraction between covalently bonded H-atom of one molecule and the electronegative atom (F or N or O) of the other molecule.
16. **Resonance:** When a molecule is represented by more than one electronic arrangement none of which is able to explain the observed characteristics of the molecule, then the actual structure is intermediate of various electronic arrangements and is known as resonance hybrid. The various electronic arrangements are called resonating structures or canonical structure.
17. **Molecular Orbital Theory (MOT):** According to this theory, in molecules the electrons are present in new orbitals called molecular orbitals. Molecular orbitals are not associated with a particular atom but belong to nuclei of all the atoms constituting the molecule.
18. **LCAO Method:** This is an approximate method, according to which the molecular orbitals are obtained by linear combination of atomic orbitals.

Class : 11th Chemistry
Chapter- 4: Chemical Bonding and Molecular Structure

Types:
(i). Covalent Bond: A chemical bond formed between two atoms by mutual sharing of electrons between them to complete their octet.
(ii). Ionic Bond: A chemical bond formed by complete transference of electrons from one atom to another acquire the stable nearest noble gas configuration.

Chemical Bond: Attractive forces which hold the various chemical constituents together in different chemical species.

Postulates:

- Electrons in a molecule are present in various molecular orbitals as electrons are present in atomic orbitals.
- Atomic orbitals of comparable energies and proper symmetry combine.
- Atomic orbitals is monocentric while a molecular orbital is polycentric.
- Number of molecular orbital formed is equal to number of combining molecular orbitals.
- Bonding molecular orbitals has low energy and high stability

Types of MO: σ(Sigma),π (Pi), δ (Delta)

Energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions.

Lattice Enthalpy

Molecular orbital theory

Postulates:

- Shape of molecule depends upon the number of valence shell electron pairs around central atom.
- Pairs of electrons in the valence shell repel one another.
- These pairs of electrons tend to occupy such positions in space that minimize repulsion.
- The valence shell is taken as a sphere with electron pairs localising on 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.
- When one or more resonance structures can represent a molecule, VSEPR model is applicable:
- **Decreasing order of repulsive interaction:**

lp–lp > lp – bp > bp –bp

Valence Bond Theory: Given by L Pauling. It explains that a covalent bond is formed between two atoms by overlap of their half-filled valance orbitals, each of which contains one unpaired electron.

Orbital Overlap Concept: Formation of a covalent bond results by pairing of electrons in valence shell with opposite spins.

Types of Overlapping: (i) Sigma σ bond – end to end.
(ii) Pi (TT) bond – axis remain parallel to each other.

Hybridisation: Process of intermixing of orbitals of different energies resulting in formation of new set of orbitals of equivalent energies and shape.

Types of Hybridisation: (i) sp (ii) sp^2 (iii) sp^3

Bonding Molecular Orbitals: Addition of atomic orbitals. **Antibonding Molecular Orbitals:** Substraction of atomic orbitals.

Chemical Bonding and Molecular Structure

Kossel Lewis approach to chemical bonding:
Lewis pictured the atom as a positively charged 'kernel' and the outer shell accommodates a maximum of eight electrons.

- Lewis postulated that atoms achieve the stable octet when linked by chemical bonds.
- Kossel gave following facts:

In the periodic table, highly electronegative halogens and highly electropositive alkali separated by noble gases.
Formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with gain and loss of electron by respective atoms.
Negative and positive ions formed attain noble gas electronic configurations.

- Negative and positive ions are stabilized by electrostatic attraction.

Octet Rule: Atoms can combine either by transfer of valence electrons from one atom to another or by sharing of valence electrons to complete octet in their valence shells.
Lewis Dot Structure provides a picture of bonding in molecules and ions in terms of the shared pairs of electrons and the octet rule.

How To Write A Lewis Dot Structure:
Step 1: Add the valence electrons of the combining atoms to obtain total number of electrons.
Step 2: For anions, each negative charge means addition of one electron. For cations, each positive charge means subtraction of one electron from total number of valence electrons.
Step 3: Write chemical symbols of combining atoms.
Step 4: Least electronegative atom occupies central position.
Step 5: After accounting for shared pairs of electrons remaining are either utilized for multiple bonding or remain as lone pairs.
Formal Charge = (Total number of valence electrons in free atom) – (Total number of non-bonding electrons) – 1/2(Total number of bonding electrons)

Limitations Of Octet Rule:

- Shows three types of exceptions (ie) incomplete octet of central atom, odd-electron molecules and expanded octet.
- Does not account for the shape of molecules.
- Fails to explain stability of molecules.

Hydrogen Bond: Formed when the negative end of one molecule attracts the positive end of other.
Types:
(i) Intermolecular: Between two different molecules of same or different compounds.
(ii) Intramolecular: H atom is between two highly electronegative atoms.

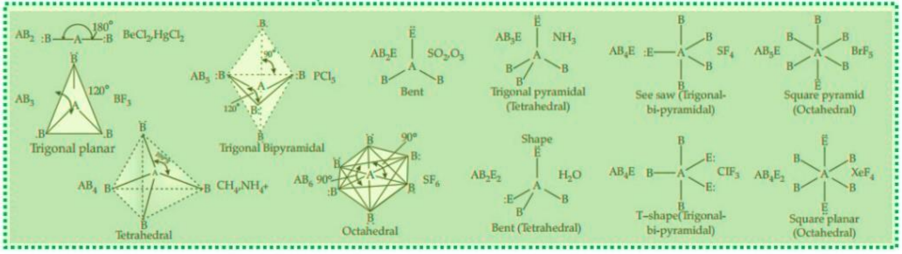
Valence Shell Electron Pair Repulsion (VSEPR)

Chemical Bonding

Hybridization

Bond Parameters

(I) Bond Length: Equilibrium distance between the nuclei of two bonded atoms in molecule.
(ii) Bond Angle: Angle between the orbitals containing bonding electron pairs around central atom in a molecule complex ion.
(iii) Bond Enthalpy: Amount of energy required to break one mole of bonds of particular type between 2 atoms.
(iv) Bond Order: Number of bonds between the two atoms of a molecule
(v) Resonance Structures: Are a set of two or more Lewis structures that collectively describe the electronic bonding a single polyatomic species.
(vi) Dipole Moment: Product of the magnitude of the charge and distance between centres of positive and negative



Important Questions

Multiple Choice questions-

1. Based on VSEPR theory, the number of 90° F-Br-F angles in BrF_5 is

   (a) 0

   (b) 2

   (c) 4

   (d) 8

2. The hybrid state of Sulphur in SO_2 molecule is:

   (a) sp^2

   (b) sp^3

   (c) sp

   (d) sp^3d

3. In allene (C_3H_4), the type(s) of hybridization of the carbon atoms is (are)

   (a) sp and sp^3

   (b) sp and sp^2

   (c) Only sp^2

   (d) sp^2 and sp^3

4. The state of hybridization of the central atom and the number of lone pairs over the central atom in POCl3 are

   (a) sp, 0

   (b) sp^2, 0

   (c) sp^3, 0

   (d) dsp^2, 1

5. The charge/size ratio of a cation determines its polarizing power. Which one of the following sequences represents the increasing order of the polarizing order of the polarizing power of the cationic species, K^+, Ca^{2+}, Mg^{2+}, Be^{2+}?

   (a) $Ca^{2+} < Mg^{2+} < Be^+ < K^+$

   (b) $Mg^{2+} < Be^{2+} < K^+ < Ca^{2+}$

   (c) $Be^{2+} < K+ < Ca^{2+} < Mg^{2+}$

   (d) $K+ < Ca^{2+} < Mg^{2+} < Be^{2+}$

6. Which one of the following does not have sp^2 hybridized carbon?

   (a) Acetone

   (b) Acetic acid

   (c) Acetonitrile

   (d) Acetamide

7. Which one of the following is paramagnetic?

   (a) NO+

   (b) CO

   (c) O_2^-

   (d) CN

8. Which of the following structures will have a bond angle of 120° around the central atom?

   (a) Linear

   (b) Tetrahedral

   (c) Triangular

   (d) Square planar

9. An atom of an element A has three electrons in its outermost orbit and that of B has six electrons in its outermost orbit. The formula of the compound between these two will be

   (a) $A_3 B_6$

   (b) $A_2 B_3$

   (c) $A_3 B_2$

   (d) $A_2 B$

10. In which of the following, the angle around the central atom is largest?

    (a) CS_2

    (b) SF_4

    (c) SO_2

    (d) BBR_3

11. Based on lattice enthalpy and other considerations which one the following alkali metals chlorides is expected to have the higher melting point?

    (a) RbCl

    (b) KCl

    (c) NaCl

    (d) LiCl

12. In which of the following substances, the intermolecular forces are hydrogen bonds?

    (a) Hydrogen Chloride

    (b) Hydrogen Sulphide

    (c) Dry Ice

    (d) Ice

13. Which one of the following pairs of species have the same bond order?
    (a) CN^- and NO^+
    (b) CN^- and CN^+
    (c) $O2^-$ and CN^-
    (d) NO^+ and CN^+
14. Dipole-induced dipole interactions are present in which of the following pairs?
    (a) H_2O and alcohol
    (b) Cl_2 and CCl_4
    (c) HCl and He atoms
    (d) SiF_4 and He atoms
15. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms is (are)
    (a) Sp and sp^3
    (b) Sp and sp^2
    (c) Only sp^2
    (d) sp^2 and sp^3

Very Short Questions:

1. What change in energy takes place when a molecule is formed from its atoms?
2. Arrange the following in order of increasing bond strengths.
3. Name the shapes of the following molecules: CH_4, C_2H_2, CO_2.
4. Arrange the following in order of increasing strengths of hydrogen bonding O, F, S, Cl, N
5. Identify the compound/compounds in the following in which S does not obey the Octet rule: SO_2, SF_2, SF_4, SF_6.
6. Name one compound each involving sp^3, sp^2, sp hybridization.
7. s-s, s-p, p-p form a bond, and only p-p form π bond.

Short Questions:

1. Which out of CH_3F and CH_3Cl has a higher dipole moment and why?
2. Define the term chemical bond. What are its different types?
3. Why covalent bonds are called directional bonds whereas ionic bonds are called non-directional?
4. AlF_3 is a high melting solid whereas SiF4 is a gas. Explain why?
5. Using the VSEPR theory identifies the type of hybridization and draw the structure of OF_2 What are oxidation states of O and F?
6. Account for the following: The experimentally determined N-F bond length in NF_3 is greater than the sum of the single covalent radii of N and F.

Long Questions:

1. State with reasons, which is more polar CO_2 or N_2O?
2. Out of peroxide ion (O_2) and superoxide ion (O_2) which has larger bond length and why?
3. Explain the formation of the following molecules according to the orbital concept, F2, HF, O_2, H_2O, N_2, NH_3 molecules.
4. What is a hydrogen bond, what are its causes, and give the conditions for hydrogen bonding? What is the strength of hydrogen bonding? Describe the two types of hydrogen bonding.

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): Sodium chloride formed by the action of chlorine gas on sodium metal is a stable compound.

   Reason (R): This is because sodium and chloride ions acquire octet in sodium chloride formation.

   (i) A and R both are correct, and R is the correct explanation of A.
   (ii) A and R both are correct, but R is not the correct explanation of A.
   (iii) A is true but R is false.
   (iv) A and R both are false.
2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): Though the central atom of both NH3 and H_2O molecules are sp3 hybridised, yet H–N–H bond angle is greater than that of H–O–H.

Reason (R): This is because nitrogen atom has one lone pair and oxygen atom has two lone pairs.

(i) A and R both are correct, and R is the correct explanation of A.

(ii) A and R both are correct, but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) A and R both are false.

Case Study Based Question:

1. Read the passage given below and answer the following questions:

Chemical bonding, involve interactions that account for the association of atoms into molecules, ions, crystals, and other stable species that make up the familiar substances of the everyday world. When atoms approach one another, their nuclei and electrons interact and tend to distribute themselves in space in such a way that the total energy is lower than it would be in any alternative arrangement. If the total energy of a group of atoms is lower than the sum of the energies of the component atoms, then bond together and the energy lowering is the bonding energy.

The ideas that helped to establish the nature of chemical bonding came to fruition during the early 20th century, after the electron had been discovered and quantum mechanics had provided a language for the description of the behaviour of electrons in atoms. However, even though chemists need quantum mechanics to attain a detailed quantitative understanding of bond formation, much of their pragmatic understanding of bonds is expressed in simple intuitive models. These models treat bonds as primarily of two kinds-namely, ionic and covalent.

The type of bond that is most likely to occur between two atoms can be predicted on the basis of the location of the elements in the periodic table, and to some extent the properties of the substances so formed can be related to the type of bonding.

A key concept in a discussion of chemical bonding is that of the molecule. Molecules are the smallest unit of compounds that can exist. One feature of molecules that can be predicted with reasonable success is their shape. Molecular shapes are of considerable importance for understanding the reactions that compounds can undergo, and so the link between chemical bonding and chemical reactivity is discussed briefly in this article.

(1) According to molecular orbital theory, which of the following will not be available molecule?

(a) He_2^{2+}

(b) He_2^+

(c) H_2^-

(d)) H_2^{2-}

(2) Which of the following compounds of chlorine contains both ionic as well as covalent bonds?

(a) NaCl

(b) $NaClO_4$

(c) PCl_3

(d) $POCl_3$

(3) In PO_4^{3-}, the formal charge on each oxygen atom and P ─ O bond order respectively are:

(a) - 0.75, 1.25

(b) - 0.75, 1.0

(c) - 0.75, 0.6

(d) - 3, 1.25

(4) On the basis of valence bond theory, the formation of H_2 molecules from two H-atoms involves.

(a) The overlap of vacant is orbitals of two H-atom

(b) The lowering of potential energy of the system as the two H-atom come near to each other

(c) The maximum energy of the system at the equilibrium internuclear distance

(d) Stabilisation of the molecule; when the nuclei are brought still closer to each other from the equilibrium inter-nuclear distance.

2. Read the passage given below and answer the following questions:

In order to explain the shapes of molecules adequately, Sidgwick and Powell in 1940 proposed a theory based on the repulsive interaction of the electron pairs in the valence shell of the atoms.

Nyholm and Gillespie (1950) further developed and redefined the concept. The mai postulates of this theory are as follows:

The number of valence shell electron pairs (bonded or non-bonded) present around the central atom decides the shape of the molecules. The shared electron pairs are called bond pairs and unshared or non-bonding electrons are called lone pairs. Electron pairs of valence shell repel one another because their electron clouds are negatively charged.

These electron pairs arrange themselves in such a way so that there is minimum repulsion and maximum distance in between them. The valence shell is considered as a sphere in which the electron pairs are localised on the spherical surface at maximum distance from one another.

A lone pair occupies more space than a bonding pair, since it lies closer to the central atom. This means that the repulsion between the different electron pairs follow the order:

Lone pair-lone pair > lone pair-bond pair > bond pair-bond pair

$$(lp - lp) > (lp - bp) > (bp - bp)$$

(1) Which of the following molecule has net dipole moment zero?
 (a) HF
 (b) H_2O
 (c) BF_3
 (d) $CHCl_3$

(2) Which one of the following species contains three bond pairs and one lone pair around the central atom?
 (a) H_2O
 (b) BF_3
 (c) NH_2^-
 (d) PCl_3

(3) Why do the deviations occur from idealised shape of H_2O and NH_3 molecules?
 (a) Same hybridisation
 (b) Different hybridisation
 (c) Repulsive effect
 (d) None of the above

(4) The species, having bond angles of 120° is:
 (a) PH_3
 (b) ClF_3
 (c) NCl_3
 (d) BCl_3

Answer Key

MCQ

1. (a) 0
2. (a) Sp^2
3. (b) Sp and sp^2
4. (c) sp^3, 0
5. (d) $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$
6. (c) Acetonitrile
7. (c) O_2^-
8. (c) Triangular
9. (b) A_2B_3
10. (b) SF_4
11. (c) NaCl
12. (d) Ice
13. (d) NO^+ and CN^+
14. (c) HCl and He atoms
15. (b) sp and sp^2

Very Short Answer:

1. There is a fall in energy.
2. $F_2 < Cl_2 < O_2 < N_2$
3. CH_4: Tetrahedral; C_2H_2: Cylindrical; CO_2: linear
4. Cl < S < N < O <F.
5. SF_4, SF_6.
6. sp^3: CH_4: sp^2: C_2H_4: sp: C_2H_2
7. s-s, s-p, p-p form a bond, and only p-p form π bond.

Short Answer:

1. **Ans:** The dipole moment of CH_3Cl is greater than that of CH_3F. The C-F bond length in CH_3F is smaller than the C-Cl bond length in CH_3Cl. The charge separation in the C-F bond is more than in the Cl-C bond- fluoride being more electronegative than chlorine. The bond length has a greater effect than the charge separation. Hence the dipole moment of CH_3C1 is greater than that of CH_3F.

2. **Ans:** The attractive forces which hold the constituent atoms in molecules or species in lattices etc. are called a chemical bond.

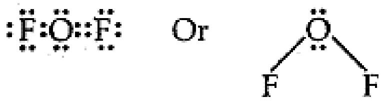
   They are of the following types:

   1. Electrovalent or ionic bond
   2. Covalent bond
   3. Coordinate or dative bond
   4. metallic bond
   5. hydrogen bond
   6. van der Waals forces.

3. **Ans:** A covalent bond is formed by the overlap of half-filled atomic orbitals which have definite directions. Hence covalent bond is directional. In ionic compounds, each ion is surrounded by a number of oppositely charged ions and hence there is no definite direction.

4. **Ans:** AlF_3 is an ionic solid due to the large difference in electronegativities of Al and F whereas SiF_4 is a covalent compound and hence there are only weak van der Waal's forces among its molecules.

5. **Ans:** The electron dot structure of OF_2 is



   Thus, the central atom (O-atom) has 4 pairs of electrons (2 bond pairs and 2 lone pairs). Hence oxygen in OF_2 is sp^3 hybridized and the molecule is V-shaped oxidation state of F = – 1, oxidation state of O = + 2.

6. **Ans:** This is because both N and F are small and hence have high-electron density. So, they repel the bond pairs thereby making the N-F bond length larger.

Long Answer:

1. **Ans:** N_2O is more polar than CO_2 which is a linear molecule and thus symmetrical. Its net dipole moment is zero.

   N_2O is linear but unsymmetrical. It is a resonance hybrid of the following canonical structures:

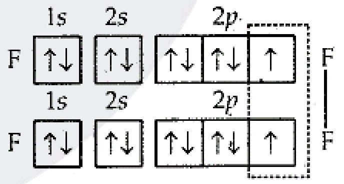
   It has a net dipole moment of 0.116 D.

2. **Ans:** The bond order of O_2^- is 1.5 while that of O_2^{2-} is 1.0.

   The lesser the bond order, the greater is the bond length as the bond order is inversely proportional to bond length. (Hence O_2^{2-} has a larger bond length than O_2^{2-}.

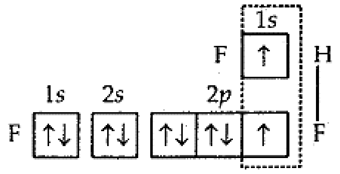
3. **Ans:**

   1. Formation of F_2 molecule. Atomic number (Z) of fluorine is 9 and its orbital electronic configuration is $1s^2\ 2s^2\ 2p^2x,\ 2p^2y,\ 2p^1z$. Thus, a fluorine atom has one half-filled atomic orbital. Therefore, two atoms of fluorine combine to form the fluorine molecule as a result of the combination for their half-filled atomic orbitals shown in Fig. The two atoms get linked by a single covalent bond

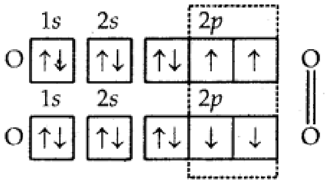


Formation of F_2 molecule

   2. Formation of HF molecule. Fluorine atom, as stated above, has one half-filled atomic orbital. Hydrogen atom (Z = 1) has only one electron in Is orbital. Thus, the hydrogen fluoride (HF) molecule. is formed as a result of the combination (or overlap) of the half-filled orbitals belonging to the participating atoms.



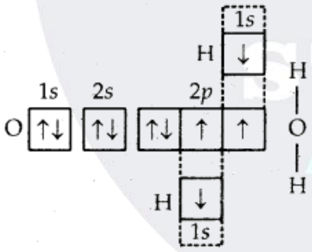
3. Formation of O_2 molecules. The atomic number (Z) of oxygen is 8 and its orbital electronic configuration is $1s^2$ $2s^2$ $2p^2x$ $2p^1x$ $2p^1z$. This means that an oxygen atom has two half-filled orbitals with one electron each. Two such atoms will combine to form a molecule of oxygen as a result of the overlap of the half-filled orbitals with opposite spins of electrons.



Formation of O_2 molecule

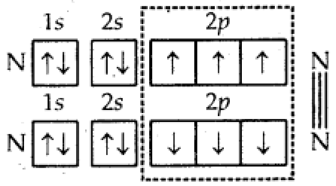
Thus, the two atoms of oxygen are bonded to each other by two covalent bonds or double bonds (O = O).

4. Formation of H_2O molecule. In the formation of the H_2O molecule, the two half-filled orbitals of the oxygen atom combine with the half-filled orbitals (1s) of the hydrogen atoms. Thus, the oxygen atom gets linked to the two hydrogen atoms by single covalent bonds as shown in



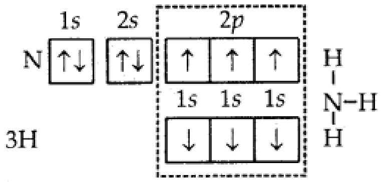
Formation of H_2O molecule

5. Formation of N_2 molecule. The atomic number of nitrogen is 7 and its orbital electronic configuration is $1s^2$ $2s^2$ $2p^1x$ $2p^1y$ $2p^1$ z. This shows that the nitrogen atom has three half-filled atomic orbitals. Two such atoms combine as a result of the overlap of the three half-filled orbitals and a triple bond gets formed (N = N)



Formation of N_2 molecule

6. Formation of NH_3 molecule. In the formation of ammonia (NH_3) molecule, three half-filled orbitals present in the valence shell of nitrogen atom combine with 1s orbital of three hydrogen atoms with one electron each. As a result, the nitrogen atom completes its octet and a molecule of NH_3 is formed in which the nitrogen atom is linked to three hydrogen atoms by covalent bonds.



Formation of NH_3 molecule

4. **Ans:** When hydrogen is connected to small highly electronegative atoms such as F, O, and N in such cases hydrogen forms an electrostatic weak bond with an electronegative atom of the second molecule, this type of bond binds the hydrogen atom of one molecule and the electronegative atom of the 2nd molecule is called as hydrogen bond. It is a weak bond and it is denoted by dotted lines e.g., in HF, hydrogen forms a weak bond with the electronegative F atom of the 2nd molecule neighboring HF.

$$\overset{\delta+}{H}-\overset{\delta-}{F}\ldots\ldots\overset{\delta+}{H}-\overset{\delta-}{F}\ldots\ldots\overset{\delta+}{H}-\overset{\delta-}{F}$$

So, it means hydrogen is acting as a bridge between two molecules by one covalent bond and the other by a hydrogen bond. Due to this hydrogen bonding, HF will not exist as a single molecule but it will exist as an associated molecule $(HF)n$. So hydrogen bond may be defined as a weak electrostatic bond that binds the hydrogen atom of one molecule and electronegative bond atoms (F, O, N) of the second neighboring molecule.

Cause of hydrogen bonding: When a hydrogen atom is bonded to an electronegative atom (say F, O, N) through a covalent bond, due to electronegativity difference, the electronegative atom attracts the shared pair of electrons towards its side with a great force as a result of which the shared pair of electrons will be displaced toward electronegative atom and away from a hydrogen atom.

Due to which hydrogen atom will acquire a slightly negative charge and if another molecule is brought nearer to it in such a way that electronegative atom of the second molecule faces hydrogen atom of the 1st molecule, due to opposite charges present on the atoms, an electrostatic bond will be formed between the hydrogen atom of one molecule and electronegative atom of 2nd molecule and this is called as hydrogen bond.

$$\overset{\delta+}{H}-\overset{\delta-}{F}.....\overset{\delta+}{H}-\overset{\delta-}{F}.....\overset{\delta+}{H}-\overset{\delta-}{F}$$

Conditions for hydrogen bonding. The following two necessary conditions for hydrogen bonding are:

1. Hydrogen atom should be connected to highly electronegative atom say F, O, or N.
2. The electronegative atom of which the hydrogen atom is connected should be the same in size.

   The smaller The size of the electronegative atom greater will be the attraction of that atom for shared pair of electrons and hence that pair will be displaced more nearer to that atom and hence that atom will develop greater negative charge and the hydrogen atom will develop a greater positive charge and hence hydrogen atom of this molecule will easily attract negative atom of the Ian molecule and hence a hydrogen bond will be easily formed.

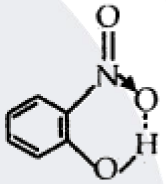
   As both these conditions are satisfied only by F, O, N atoms so only three atoms show hydrogen bond.

   Strength of Hydrogen Bond: A hydrogen bond is a very weak bond. It is weaker than an ionic or a covalent bond. Its strength ranges from 13 kJ mol-1 to 42 kJ mol^{-1}. The strength of the hydrogen bond for some of the molecules is the order H-F H (40 kJ mol-1) > O-H…… O (28 kJ mol^{-1}) > H-N…… H (13 kJ mol^{-1}) whereas the strength of a covalent bond is quite high. For example, the bond strength of the H-H bond in H_2 is 433 kJ mol^{-1}

Types of H-bonding

There are two types of hydrogen-bonds

1. Intermolecular hydrogen bond. It is formed between two different molecules of the same or different compounds. For example, H-bond in case of HF, alcohol, or water.
2. Intramolecular Hydrogen bond. It is formed when a hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule. For example, in o-nitrophenol, hydrogen is in between the two oxygen atoms.



Assertion Reason Answer:

1. (i) A and R both are correct, and R is the correct explanation of A.
2. (i) A and R both are correct, and R is the correct explanation of A.

Case Study Answer:

1. **Answer:**
   (1) (d) H_2^{2-}
   (2) (b)$NaClO_4$
   (3) (a) - 0.75, 1.25
   (4) (b) The lowering of potential energy of the system as the two H-atom come near to each other
2. **Answer:**
   (1) (c) BF_3
   (2) (d) PCl_3
   (3) (c) Repulsive effect
   (4) (d) BCl_3

❖❖

States of Matter

5

Introduction

Gas is the state of matter in which molecules are always in random motion. Intermolecular interactions are extremely small (almost negligible) as compared to other states like solid and liquid. Gases are highly compressible state of matter and its state of diffusion is maximum. Gases have their own importance in living world. Air is a gaseous mixture of oxygen, nitrogen, CO_2, Ar, etc.

Intermolecular Forces

Intermolecular forces are the forces of attraction and repulsion between interacting particles. This term does not include the electrostatic forces that exist between the two oppositely charged ions.

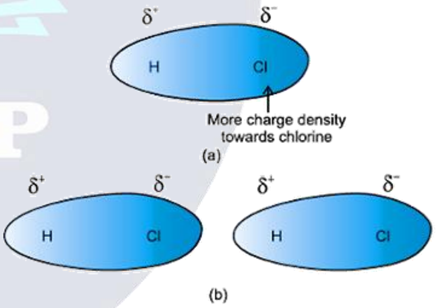
Van der Waal's Forces

These are the weak forces of attraction between two molecules with or without any strong bond. These are electrostatic in nature. Types of van der Waal's forces are as follow:

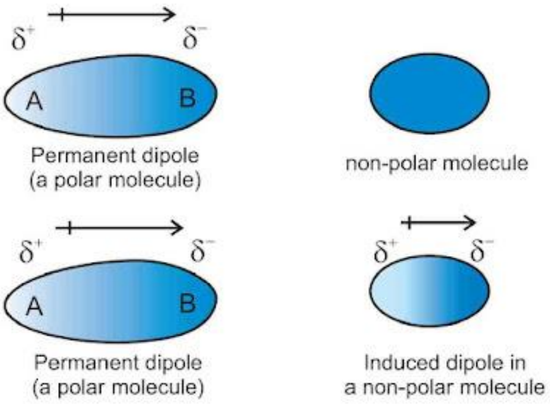
1. **Dipole-dipole interaction:** These forces exist between two molecules which are polar in nature. Opposite charges of two dipoles attract each other and produce interactions called keesom forces. In HCl, dipole-dipole interactions exist.

   Dipole-dipole interaction energy is inversely proportional to the sixth power of the distance between the rotating polar molecules.

$$\text{interaction energy} \propto \frac{\pi}{r^6}$$



2. **Dipole-induced dipole interaction:** When a polar molecule comes closer to a non-polar molecule it induces weak polarity (dipole) in that molecule. Now, weak interactions develop between polar molecule and molecule in which polarity is induced. These interactions are known as Debye interactions.



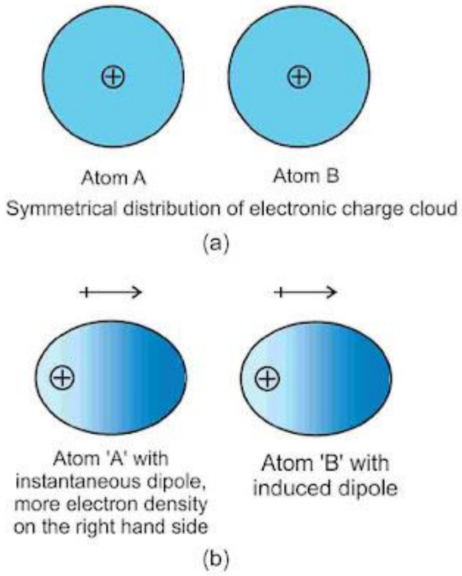
Permanent dipole (a polar molecule)

non-polar molecule

Permanent dipole (a polar molecule)

Induced dipole in a non-polar molecule

3. **London dispersion forces:** This polar molecule produces polarity in another molecule. Weak interaction arises between instantaneous dipoles. These interactions are known as Dispersion forces or London forces.



Measurable Properties of Gases

1. **Temperature:** Temperature is a relative measure, or indication of hotness or coldness. At absolute zero on Kelvin scale is equivalent to –273.15°C on the Celsius scale. Both the Celsius and the Kelvin scales have units of equal magnitude that is one degree celsius equivalent to one kelvin.

   Thus T(K) = T(°C) + 273.15

2. **Pressure of a gas:** According to laws of motion, pressure is defined as force applied per unit area of surface. It is denoted by P and SI unit of it is pascal (Pa). It is a scalar quantity.

$$P = \frac{F}{A}$$

3. **Atmospheric Pressure:** The atmospheric pressure at a point is equal to the weight of a column of air of unit cross-sectional area extending from that point to the top of the atmosphere. Its value is 1.013×10^5 Pa at sea level. Atmospheric pressure is measured using an instrument called barometer.

Gaseous Laws

Boyle's Law (Volume-Pressure Relation)

According to this, "The volume of a given mass of gas is inversely proportional to pressure at constant temperature." This law is given by Robert Boyle.

$$P \propto \frac{1}{v} \dots\dots \text{(at Constant T and n)}$$

$$P = k\frac{1}{v}$$

where k is the proportionality constant.

If a fixed amount of gas at constant temperature T occupying volume V_1 at pressure P_1 undergoes expansion, so that volume becomes V_2 and pressure becomes P_2, then according to Boyle's law:

$P_1V_1 = p_2V_2$ = constant

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

Charle's Law (Volume-Temperature Relation)

According to this, "The volume of a given mass of gas is directly proportional to its absolute temperature at constant pressure." This law is given by Jacques Charles.

$$V \propto T \text{ .... (at constant P)}$$

$$V = k\,T$$

where k is the proportionality constant.

If a fixed amount of gas at constant pressure P occupying volume V_1 at temperature T_1 undergoes expansion, so that volume becomes V_2 and temperature becomes T_2, then according to Charle's Law:

$$\frac{V}{T} = \cdots \ldots \ldots \ldots .. \text{constant}$$

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

Gay Lussac's Law (Pressure-Temperature Relation)

It states that at constant volume, the pressure of a fixed mass of a gas is directly proportional to the Kelvin temperature. The law may be expressed mathematically as

$$P \propto T \text{ .... (at constant V)}$$

$$P = k\,T$$

where k is the proportionality constant.

If a fixed amount of gas at constant volume V occupying pressure P_1 at temperature T_1 undergoes expansion, so that pressure becomes P_2 and temperature becomes T_2, then according to Gay Lussac's Law:

$$\frac{P}{T} = \text{constant}$$

$$\frac{P_1}{T_1} = \frac{P_2}{P_2}$$

Avogadro's Law ((Volume - Amount Relationship)

According to this, "Equal volumes of all gases at same temperature and pressure contain equal numbers of molecules".

$$V \propto n$$

$$V = k\,n$$

where k is the proportionality constant.

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

Ideal Gas Equation

On combining the Boyle's law, Charles law and Avogadro's law we get an equation known as ideal gas equation which correlate P, V, T of a gas.

$$V \propto \frac{1}{P} \text{ (according to Boyle's law at constant T)}$$

$V \propto T$ (according to Charle's law at constant P)

$$V \propto n \text{ (according to Avogadro's law at constant P and T)}$$

$$V \propto \frac{nT}{P}$$

$$PV \propto nT$$

$$PV = nRT$$

Where R is proportionality constant known as universal gas constant.

Numerical value of R:

- $R = 0.0821$ litre atm K^{-1} mol^{-1}
- $R = 0.0831$ litre bar K^{-1} mol^{-1}
- $R = 8.314$ J K^{-1} mol^{-1}
- $R = 1.987 \approx 2$ cal K^{-1} mol^{-1}

- R = 8.314 × 107 erg K^{-1} mol^{-1}

If temperature, volume and pressure of a fixed amount of gas vary from T_1, V_1 and p_1 to T_2, V_2 and p_2 then we can write

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

This equation is also known as Combined gas law.

Dalton's Law of Partial Pressure

Dalton's law of partial pressure and states that "the total pressure exerted by a mixture of non reacting gases is equal to the sum of partial pressure of each gas present in the mixture".

Total = $p_1 + p_2 + p_3$ +......(at constant T, V)

Kinetic Theory of Gases

The postulates of kinetic theory of gases are as follows:

1. The gaseous molecules are considered to be point masses.
2. The volume of a molecule is negligible as compared to total volume of the gas.
3. The molecules neither attract nor repel each other.
4. The collisions are perfectly elastic i.e. there is no loss of energy during the molecular collisions.
5. The average kinetic energy of molecules is directly proportional to the absolute temperature of the gas.
6. The effect of gravity on molecular motion is negligible.

The Kinetic Gas Equation

where P =Pressure of the gas

$$PV = \frac{1}{3}mv^2$$

V = Volume of the gas

m = Mass of one molecule of a gas

n = number of molecules of gas

u = root mean square speed of the molecule

m × n = M = molecular weight of the gas.

$$PV = \frac{1}{3}Mu^2$$

Graham's Law of Diffusion

According to Graham's Law "at constant pressure and temperature, the rate of diffusion or effusion of a gas is inversely proportional to the square root of its vapour density or molecular mass".

$$r \propto \sqrt{\frac{1}{d}}$$

Behaviour of Real gases

Ideal gas: A gas which obeys the gas laws and the gas equation PV = nRT strictly at all temperatures and pressures is said to be an ideal gas. But actually, the concept of ideal gas is hypothetical as there is no gas which practically is ideal. So, the non-ideal gases are the real gases which are the actually existing gases which obey gas equation approximately only under two conditions.

(i) Low pressure.

(ii) High temperature.

Causes of Deviation

There are two hypothetical postulates in the kinetic theory of gases. These are as follows:

1. The volume of a molecule is negligible as compared to total volume of the gas. Actually, gas molecules do possess some volume which account for the deviation.

2. There is no intermolecular forces of attraction between gaseous molecules.

   By correcting these two postulates, we get an equation which can be applied to the gases which deviate from ideal behaviour. This deviation of a gas from ideal behaviour can also be expressed in terms of compressiblity factor (Z).

$$Z = \frac{PV}{RT}$$

Van der Waal's Equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT\ A = \pi r^2$$

Where a and b are van der waal's constant.

Liquefaction of Gases

Gases can be liquefied by applying high pressure or by cooling.

Critical Temperature: It is the temperature above which gas cannot be liquefied, no matter how high be pressure.

$$T_c = \frac{8a}{27Rb}$$

Critical Pressure: It is the minimum pressure that is required to liquefy a gas at critical temperature.

$$P_c = \frac{a}{27b^2}$$

Critical Volume: It is the volume occupied by gas at critical temperature and critical pressure.

$$Vc = 3b$$

1. **Liquid State:**

   It is the intermediate state between gaseous and solid states. Liquids possess fluidity like gases but incompressibility like solids.

   Properties of liquid are:

   a. A liquid is made up of molecules. Only Hg(l) is in atomic state.

   b. The intermolecular forces of attraction in a liquid are quite large.

   c. Liquids have no definite shape but have definite volume as the cohesive forces are strong.

   d. Liquids diffuses slowly in comparison to gas.

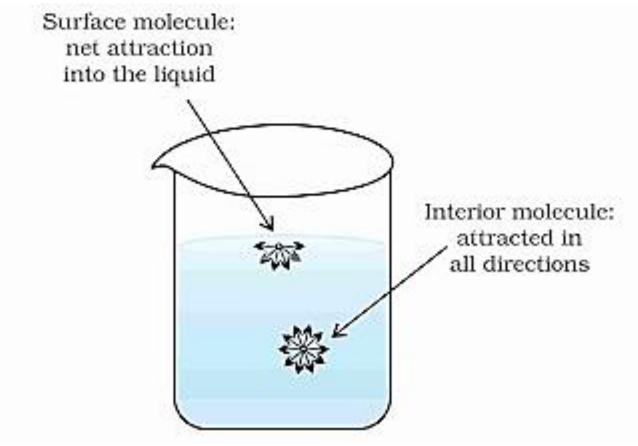
   e. They have definite volume but irregular shapes or we can say that they can take the shape of the container.

2. **Evaporation:** The process of change of liquid into vapour state at any given temperature is evaporation. Evaporation is accompanied by cooling as average kinetic energy of remaining molecules decreases. Example: Ether evaporates faster than alcohol.

3. **Vapour Pressure:** In a closed vessel when the rate of evaporation become equal to rate of condensation, i.e. equilibrium is established, the pressure exerted by the vapours of liquid on its on surface is known as vapour pressure.

4. **Boiling Point:** Boiling point of the liquid is the temperature at which the vapour pressure of the liquid is equal to the atmospheric pressure. Ex- Boiling point of pure water is 100 °C.

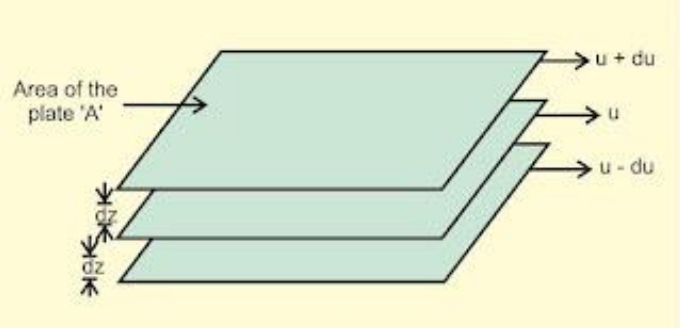
5. **Surface tension:** "It is the force acting on the surface at right angles to any line of unit length".



The property of surface tension may also be described in terms of the tendency of a liquid to decrease its surface area. It's SI unit is N/m.

$$\text{Surface tension, } S = \frac{F}{l}$$

6. **Viscosity:** The property of the liquids which determines their resistance to flow, is called viscosity. The forces between the layers which oppose the relative motion between them are known as the forces of viscosity. Thus viscosity may be thought of as the internal function of a fluid in motion.



$F \propto \frac{dv}{dz}$ is called velocity gradient]

$$F \propto A$$

$$F = nA\frac{dv}{dz}$$

η is the coefficient of viscosity. It is expressed in $Nm^{-2}s$ or poise

1 poise = 0.1 $Nm^{-2}s$

7. **Fluidity(Φ):** The reciprocal of the coefficient of viscosity is called Fluidity.

$$\Phi = \frac{1}{\eta}$$

1. **Three different states of matter (solid, liquid and gas):** Solid is that state of matter which has a definite shape and a definite volume, liquid has a definite volume but no definite shape whereas gas has neither definite shape nor definite volume.
2. **Two more states of matter:**
   i. Plasma state which consists of a mixture of electrons and positively charged ions formed due to super heating of gases, e.g., in sun or stars.
   ii. Super cooled solid state in which atoms lose their identity to form a single super atom.
3. **Triple point:** It is the temperature at which all the three states of matter or phases of the same substance exist together, e.g., ice, water and water vapour exist together at 0.01°C (273.16 K) and 4.58 mm pressure.
4. **Ideal and Real gases:** A gas which obeys ideal gas equation under all conditions of temperature and pressure is called an ideal gas. However, the concept of ideal gas is only hypothetical. The gases obey gas laws only if pressure is low or temperature is high. Such gases are called real gases.
5. **Significance of van der Waal's constants:** 'a' is a measure of the magnitude of attractive forces whereas 'b' is a measure of the effective size of the gas molecules. b = 4v where v is actual volume of gas molecules. 'b' is called excluded volume or co-volume.
6. **Boiling point:** It is the temperature at which vapour pressure of the liquid becomes equal to external pressure. When external pressure = 1 atm = 760 mm, it is called normal boiling point.
7. **Surface tension of liquids:** It is the force acting at right angles to the surface along one centimeter length of the surface. Its units are dynes cm–1 or Nm–1.
8. **Vapour pressure of a liquid:** It is the pressure exerted by the vapour present in equilibrium with a liquid in a closed vessel at a particular temperature. Cooling is caused by evaporation because more energetic molecules leave the liquid.
9. **Viscosity of liquids:** It is the internal resistance of a liquid to flow or it is the force of friction which one part of the liquid offers to another part of the liquid.
10. **Factors affecting viscosity:**
    i. **Nature of the liquid:** Greater the inter-molecular forces, higher is the viscosity.
    ii. **Temperature:** Viscosity of a liquid decreases with increase of temperature because kinetic energy increases and hence inter-molecular forces of attraction decrease.

11. **Boyle's law:** Temperature remaining constant, volume of a given mass of a gas is inversely proportional to its pressure, i.e., $V \propto \frac{1}{P}$ at constant T or PV = constant.
12. **Dalton's law of partial pressures:** If two or more gases which do not react chemically with each other are enclosed in a vessel, then total pressure exerted by the gaseous mixture is the sum of their partial pressure.
13. **Graham's law of diffusion/effusion:** Under similar conditions of temperature and pressure, rates of diffusion/effusion of different gases are inversely proportional to the square root of their densities.
14. **Compressibility factor (Z):** The extent of deviation of a real gas from ideal behaviour is expressed in terms of compressibility factor (Z) viz. $Z = P\frac{V}{n}RT$.

Characteristics of Gases

1) Gases have neither definite shape nor definite volume. They take up the shape and volume of the container.
2) They have lower density than liquids and solids.
3) They are highly compressible
4) Gases intermix completely in all proportion without any mechanical aid.
5) They exert pressure equally in all direction.

Measurement of mass

The mass of a gas can be easily determined by weighing the container containing the gas, and then emptying the container by taking out the gas and weighing the empty container again. The difference between the two masses gives the mass of the gas.

$$\text{number of moles}(n) = \frac{\text{mass of substance of substance}(g)}{\text{molar mass of substance}}$$

$$n = \frac{m}{M}$$

$$1 \text{ mole} = 6.022 \times 1023$$

Measurement of volume

As a gas fills the whole of the vessel in which it is put, hence the volume of the gas is equal to the volume of its container which in turn can be calculated from the dimensions of the container.

The S.I. unit of volume is m^3.

$1\ m^3 = 10^3\ dm^3 = 10^6\ cm^3$

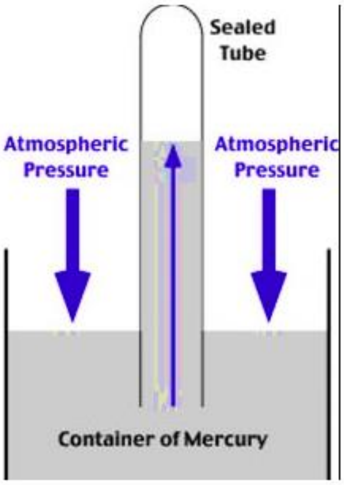
$1\ ml = 1\ cm^3$

$1\ L = 10^3\ cm^3 = 1\ dm^3 = 10^{-3}\ m^3$

Measurement of pressure

The instrument used for the measurement of atmospheric pressure is called a barometer.

It consists of inverting a tube filled with mercury in a dish of mercury. The height of the mercury column above the level of mercury in the dish is a measure atmospheric pressure at that place.

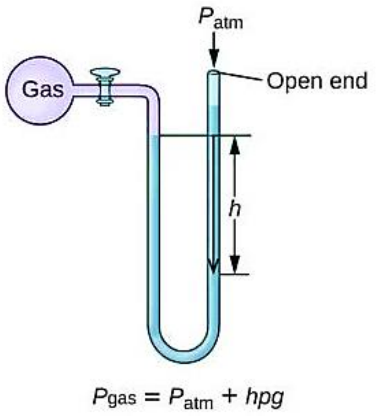


Mercury is used as a barometric liquid because

1) The height of the column in a barometer is inversely proportional to the density of the liquid. As Mercury has very high density, the height of the column setup is very convenient for study.
2) Mercury is non-volatile at room temperature. Hence, the vapour pressure due to Mercury vapour is negligible.

The instrument used for the measurement of the pressure of a gas is called manometer. It simply consists of a U- shaped tube containing mercury usually.

Two types of manometers are:



1) Those in which the longer limb is closed. Closed limb manometer is used only for gases at pressure less than the atmospheric pressure.
2) Those in which the longer limit is open. Open limb manometer is used for all.

Suppose height of the mercury column= h cm

Area of cross section of the tube= A cm^2

Volume of the mercury column= A × h cm^3

Density of mercury at room temperature= ρ g cm^{-3}

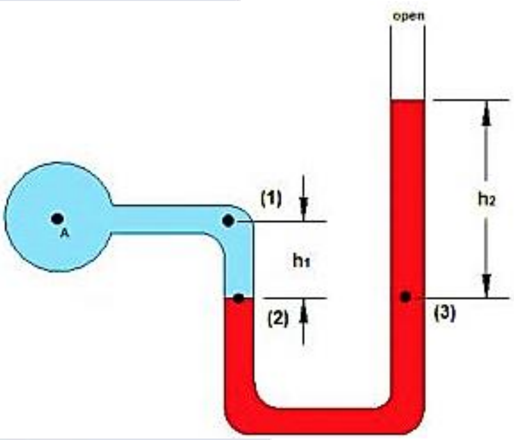
mass of mercury column=A × h × ρ grams

weight of mercury column= (A × h × ρ) × g gram

Weight of mercury column is the force acting on A cm^3.Hence

Pressure= h × ρ × g

A standard or normal atmospheric pressure is defined as the pressure exerted by a mercury column of exactly 76 cm at 0°C. This is the pressure exerted by the atmosphere at the sea level.



1 atm= 76 cm = 760 mm = 760 torr

1 atm= 1.01325 bar

1atm= 0.987 atm

The S.I. unit of pressure is pascal(Pa)

1 Pa= 1 Nm^{-2} = 1kg m^{-1} s^{-2}

1atm= 1.0132^5 × 105 Nm^{-2}

1 bar= 10^2 kPa

Measurement of temperature

Temperature is a measure of the extent of hotness or coldness of a body.

It is based on the principle that substances expand on heating.

Substance used in the measurement of temperature is mercury.

There are three different scales on which the temperature are measured

1) Fahrenheit scale
2) Kelvin scale
3) Celsius scale

$$T_k = T_C + 273.15 \quad T_C = \frac{5}{9}(T_F - 32) \quad T_F = \frac{9}{5}T_C + 32$$

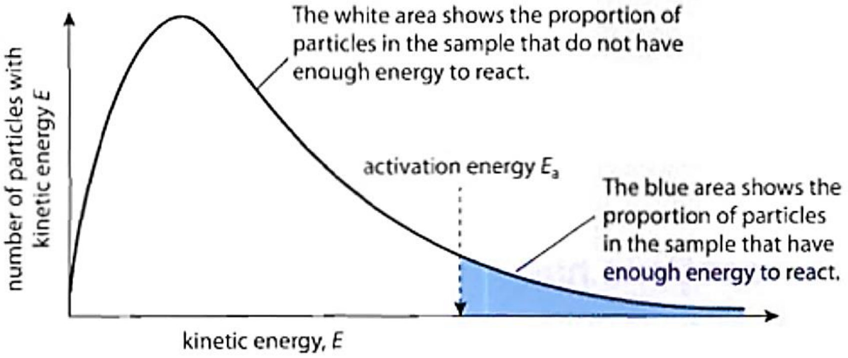
Maxwell-Boltzmann Distribution

Maxwell-Boltzmann distribution of Molecular speed

At a particular temperature, different molecules of a gas possess different speeds. Due to continues collision among the molecules themselves and against the walls of the container, their speed keep on changing.

As a result of collision, some others are speeded up, some others are slowed down and hence the fashions of molecules possessing particular speed remain constant at constant temperature.

If fractions of molecules possessing particular speed are plotted against their corresponding speeds at a particular temperature, a curve is obtained. This distribution of speed is called **maxwell-Boltzmann distribution.**



From this curve, it may observe that,

(1) Fraction of molecules having too low or too high-speed are very small.

(2) The peak of the curve corresponds to a speed possessed by the maximum fraction or maximum number of molecules. This speed is called most probable speed and is represented by c*

Effect of nature of the gas

At the same temperature, lighter gas will have higher value of most probable speed i.e. move faster than heavier gases.

For example: Distribution curve for chlorine and nitrogen gases are:

Effect of temperature

Maxwell – Boltzmann distribution curve for a gas at three different temperatures is:

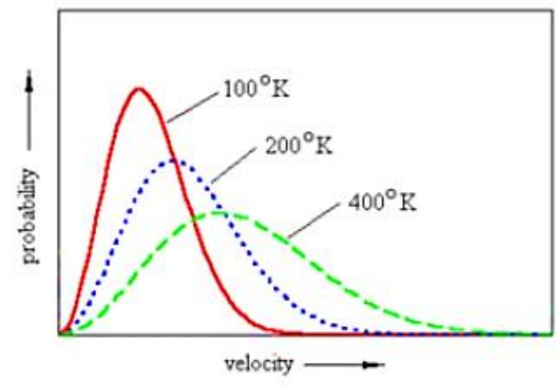
(1) The peak shift forward showing that the most probable velocity increases.

(2) The peak shift downwards showing that fraction of molecules or number of molecules possessing most probable velocity decreases.

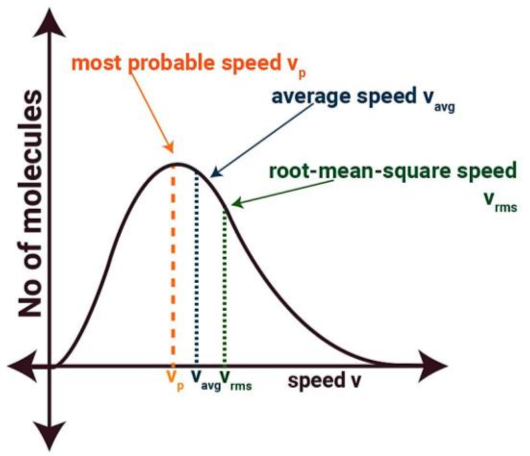
(3) The curve is flattened in the middle showing that more molecules have speeds near to the most probable speed.

(4) The fraction of molecules having higher speed increases.

(5) The fraction of molecules having lower speed decreases.



Relationship between different types of speed



Liquefaction of Gases and Critical Temperature

The liquefaction of a gas takes place when the intermolecular forces of attraction become so high that they bind the gas molecules together to form the liquid state.

The intermolecular forces of attraction can be increased either by increasing the pressure so that the molecules come close together or by cooling the gas so that the kinetic energy of the molecules decreases and they become slower.

The effect of temperature on the liquefaction of gases is found to be very important as higher the temperature of the gas, more difficult it is to liquefy it and higher is the pressure required.

Gas like hydrogen, helium, oxygen, nitrogen could not be liquefied at room temperature by application of pressure alone. Each of these gases could also be liquefied provided first it is cooled down to or below a particular temperature. For each gas, there is a particular temperature above which it cannot be liquefied, howsoever, high pressure may be applied on the gas. This temperature is called critical temperature.

Critical temperature of a gas may be defined as that temperature above which it cannot be liquefied however high pressure may be applied on the gas.

The pressure required to liquefy the gas at the critical temperature is called critical pressure.

The volume occupied by 1 mole of the gas at critical temperature and critical pressure is called critical volume.

All the three are called critical constants of the gas and are represented by Tc, Tp, Tv.

Andrews experiment on critical phenomena

Andrews in 1861 was the first to study the critical phenomena experimentally using carbon dioxide gas.

He studied the effect of pressure on the volume of carbon dioxide at different constant temperature. The plots obtained are called isotherms.

At the lowest temperature employed i.e. 13.1° C , at low pressure, carbon dioxide exist as a gas, as shown at the point A.

As the pressure is increased, the volume of the gas decreases along the curve.

The point at which liquefaction of the gas starts, volume decreases rapidly because liquid has much less volume than the gas.

Once the liquification is complete, the increase in pressure has very little effect upon volume because liquids are very little compressible. Hence a steep curve is obtained.

As the temperature is increased, horizontal portion becomes smaller and smaller and at 30.98 °C , it is reduced to a point E.

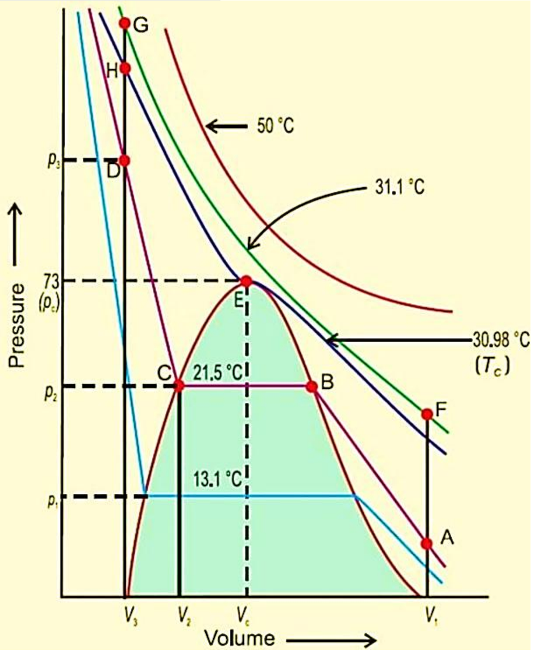
Above 30.98°C, the gas cannot be liquefied at all, however high pressure may be applied. Thus 30.98°C is the critical temperature.

We get a dome shaped curve.

A point like A represent gaseous state.

A point Like D represents a liquid state.

A point within the dome shaped area represents existence of liquid and gaseous carbon dioxide in equilibrium.



Importance of critical temperature

The critical temperature of a gas is a measure of the strength of the intermolecular forces of attraction.

Weaker are the intermolecular forces, more difficult it is to liquefy that gas and hence lower would be the critical temperature of that gas.

Helium and hydrogen have weak intermolecular forces; thus, they are difficult to liquefy and hence have low critical temperature.

Carbon dioxide and ammonia have strong intramolecular forces of attraction, they can be easily liquefied and their critical temperature are high which are above room temperature.

Van der waals constant a is also a measure of intermolecular forces of attraction. Hence it is found that the values of constant a increase in the same order as the critical temperature.

As a gas can be liquefied below the critical temperature by applying pressure. Therefore, above the critical temperature, it is a gas but below the critical temperature it is a vapour.

For ex: Carbon dioxide below its critical temperature is called carbon dioxide vapour.

Filed Under: States of Matter, Chemistry, Class 11

Tagged With: Andrews experiment on critical phenomenon, carbon dioxide vapour, critical constants, critical pressure, Critical temperature, critical volume, Importance of critical temperature, isotherms, liquefaction of a gas

You are here: Home / Class 11 / Chemistry / States of Matter / Vapour Pressure

Vapour Pressure

In a liquid, the molecules are quite close together so that there are considerable forces of attraction between them and hence they are held together in a definite volume.

The liquids possess fluidity like gases but incompressibility like solid.

Properties of Liquid

(1) ***Liquids have no definite shape:*** They take up the shape of the vessel in which they are put. This is because the molecules in a liquid are in a state of constant rapid motion.

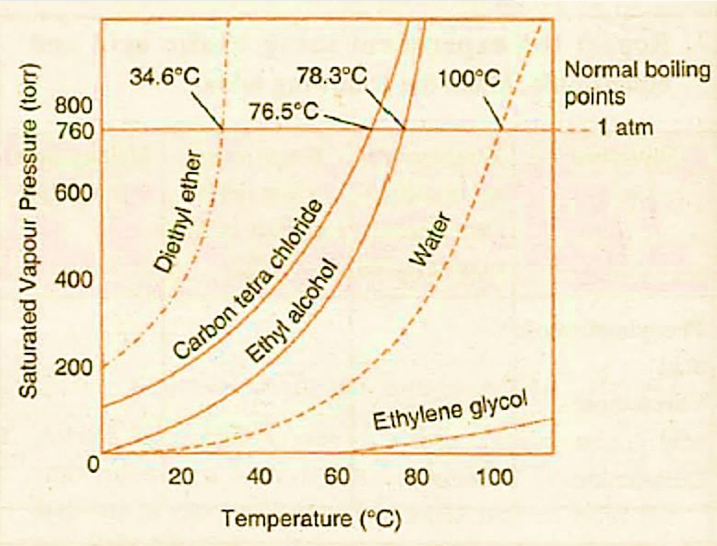
(2) ***Liquids have a definite volume:*** This is because the intermolecular forces of attraction in a liquid are quite strong and unlike gas molecules, the liquid molecules are not completely free to move.

(3) ***Liquids have much higher density than gases:*** This is because the molecules in a liquid are quiet close together. Thus, the molecules are much more closely packed than those of the gases.

(4) ***Compressibility: liquids are much less compressible than gases.*** This is because the intermolecular distances of separation are much smaller in liquid than that in gases.

(5) ***Diffusion:*** liquids diffuse like gases but the diffusion is much slower because the liquid molecules are quite close, they undergo a much larger number of collisions with each other.

Vapour Pressure



Suppose some liquid is placed in an evacuated vessel connected to a manometer. According to kinetic theory of liquids, the molecules of the liquid are constantly moving in different directions with different speeds. As these molecules are moving with different speeds, they possess different kinetic energy.

At any particular temperature, the energy of some of the molecules may be so high that they may overcome the forces of attraction by the neighbouring molecules and may leave the liquid and come in the space above the liquid. This process is called evaporation

As the time passes, more and more molecules of the liquid leave the liquid and come in space above the liquid. The molecules thus present above the liquid are called vapour. The molecules in the vapour phase are also constantly moving and some of them strike the surface of the liquid and maybe recaptured by the liquid. The process is called condensation.

If the liquid is added into the evacuated vessel, then initially, as there are no molecules of vapour, the rate of condensation is zero.

If the temperature is kept constant, the evaporation continues at constant rate as shown by the straight-line plot. With the passage of time, as a number of molecules in the vapour phase becomes more and more, the rate of condensation also increases.

A stage is reached when rate of condensation becomes equal to rate of evaporation *i.e.* as many molecules re-enter into a liquid as leave the liquid in the same time. This state is called state of equilibrium .

The pressure exerted by the vapours at this stage is called vapour pressure or saturated vapour pressure as the vapour phase is saturated with vapours at this stage.

Vapour pressure of a liquid at any temperature may be defined as the pressure exerted by the vapour present above the liquid in equilibrium with the liquid at that temperature.

Important results related with process of evaporation

(1) Cooling caused by Evaporation

When a liquid evaporates, the more energetic molecules leave the liquid. As a result the average kinetic energy of the remaining liquid decreases and hence the temperature falls.

(2) Factors affecting Vapour Pressure

(i) Nature of the liquid : If the intermolecular forces of attraction in the liquid are weak ,the molecules can easily leave the liquid and come into vapour phase and hence the vapour pressure is higher.

For example: The vapour pressure of acetone, benzene is higher than that of water at same temperature.

(ii) Effect of temperature: As the temperature of a liquid is increased, the vapour pressure of liquid increases.

(3) Boiling point

The vapour pressure of a liquid increases as the temperature is increased. The vapour escaping are only from the surface of the liquid. If the temperature is further increased till the vapour pressure becomes equal to atmospheric pressure, the vapour in the form of bubbles from below the surface start rising to the surface and escape into the air. The temperature at which this happens is called boiling point.

Boiling

Boiling point of a liquid is defined as the temperature at which the vapour pressure of the liquid becomes equals to external pressure.

When the external pressure is normal atmospheric pressure, the boiling point is called normal boiling point.

When the external pressure is equal to 1 bar, the boiling point is called standard boiling point of the liquid.

Standard boiling point of a liquid is slightly less than the normal boiling point because one bar is slightly less than 1 atmosphere pressure.

Application of effect of external pressure on boiling point

(1) If the external pressure is higher, more heat will be required to make the vapour pressure equal to external pressure and hence higher will be the boiling point. That is why in hospitals ,the surgical instruments are sterilised in autoclaves in which boiling point of water is raised by using a weigh to cover the vent.

(2) If the external pressure is decreased, the boiling point is lowered. This is the reason that a liquid boils at a lower temperature on the top of the mountain than on the sea shore. That is why at hills, use of pressure cooker is essential for cooking food.

(3) It is used for purifying the unstable liquids by distillation under reduced pressure.

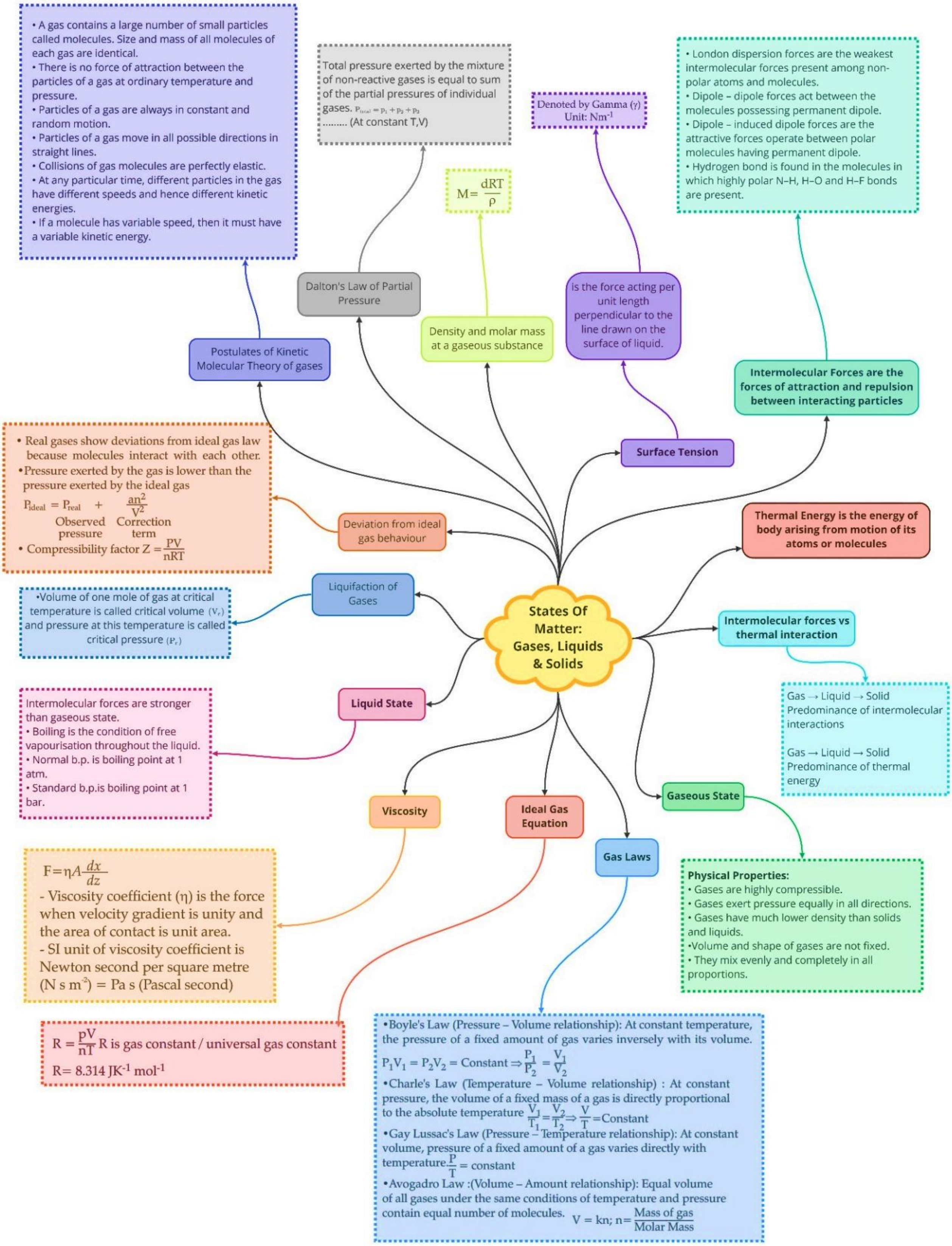
(4) Heat of Vaporisation

When the liquid starts boiling ,if extra heat is supplied to the liquid, it is used up not in increasing the temperature of the liquid but to overcome the intermolecular forces of attraction, existing in the liquid and thus changing the liquid into vapour. Hence the temperature remain constant till whole of the liquid changes into vapour.

The amount of heat required to change 1 mole of the liquid into its vapour at the boiling point is called the heat of vaporisation of the liquid.

Greater the intermolecular forces of attraction present in a liquid, greater is the heat of vaporisation and higher is the boiling point.

Class : 11th Chemistry
Chapter- 5: States Of Matter: Gases, Liquids & Solids



States Of Matter: Gases, Liquids & Solids

Postulates of Kinetic Molecular Theory of gases

- A gas contains a large number of small particles called molecules. Size and mass of all molecules of each gas are identical.
- There is no force of attraction between the particles of a gas at ordinary temperature and pressure.
- Particles of a gas are always in constant and random motion.
- Particles of a gas move in all possible directions in straight lines.
- Collisions of gas molecules are perfectly elastic.
- At any particular time, different particles in the gas have different speeds and hence different kinetic energies.
- If a molecule has variable speed, then it must have a variable kinetic energy.

Dalton's Law of Partial Pressure

Total pressure exerted by the mixture of non-reactive gases is equal to sum of the partial pressures of individual gases. $P_{total} = p_1 + p_2 + p_3$ .... (At constant T,V)

Density and molar mass at a gaseous substance

$M = \frac{dRT}{\rho}$

Surface Tension

is the force acting per unit length perpendicular to the line drawn on the surface of liquid.

Denoted by Gamma (γ)
Unit: Nm^{-1}

Intermolecular Forces are the forces of attraction and repulsion between interacting particles

- London dispersion forces are the weakest intermolecular forces present among non-polar atoms and molecules.
- Dipole – dipole forces act between the molecules possessing permanent dipole.
- Dipole – induced dipole forces are the attractive forces operate between polar molecules having permanent dipole.
- Hydrogen bond is found in the molecules in which highly polar N–H, H–O and H–F bonds are present.

Deviation from ideal gas behaviour

- Real gases show deviations from ideal gas law because molecules interact with each other.
- Pressure exerted by the gas is lower than the pressure exerted by the ideal gas

$$P_{ideal} = \underbrace{P_{real}}_{\text{Observed pressure}} + \underbrace{\frac{an^2}{V^2}}_{\text{Correction term}}$$

- Compressibility factor $Z = \frac{PV}{nRT}$

Thermal Energy is the energy of body arising from motion of its atoms or molecules

Liquifaction of Gases

•Volume of one mole of gas at critical temperature is called critical volume (V_r) and pressure at this temperature is called critical pressure (P_r)

Intermolecular forces vs thermal interaction

Gas → Liquid → Solid
Predominance of intermolecular interactions

Gas ← Liquid ← Solid
Predominance of thermal energy

Liquid State

Intermolecular forces are stronger than gaseous state.
- Boiling is the condition of free vapourisation throughout the liquid.
- Normal b.p. is boiling point at 1 atm.
- Standard b.p.is boiling point at 1 bar.

Gaseous State

Physical Properties:
- Gases are highly compressible.
- Gases exert pressure equally in all directions.
- Gases have much lower density than solids and liquids.
- Volume and shape of gases are not fixed.
- They mix evenly and completely in all proportions.

Viscosity

$F = \eta A \frac{dx}{dz}$

- Viscosity coefficient (η) is the force when velocity gradient is unity and the area of contact is unit area.
- SI unit of viscosity coefficient is Newton second per square metre ($N\,s\,m^{-2}$) = Pa s (Pascal second)

Ideal Gas Equation

$R = \frac{pV}{nT}$ R is gas constant / universal gas constant

$R = 8.314\ JK^{-1}\ mol^{-1}$

Gas Laws

- Boyle's Law (Pressure – Volume relationship): At constant temperature, the pressure of a fixed amount of gas varies inversely with its volume.
$P_1V_1 = P_2V_2 = \text{Constant} \Rightarrow \frac{P_1}{P_2} = \frac{V_1}{V_2}$
- Charle's Law (Temperature – Volume relationship) : At constant pressure, the volume of a fixed mass of a gas is directly proportional to the absolute temperature $\frac{V_1}{T_1} = \frac{V_2}{T_2} \Rightarrow \frac{V}{T} = \text{Constant}$
- Gay Lussac's Law (Pressure – Temperature relationship): At constant volume, pressure of a fixed amount of a gas varies directly with temperature. $\frac{P}{T} = \text{constant}$
- Avogadro Law :(Volume – Amount relationship): Equal volume of all gases under the same conditions of temperature and pressure contain equal number of molecules. $V = kn;\ n = \frac{\text{Mass of gas}}{\text{Molar Mass}}$

Important Questions

Multiple Choice questions-

1. Three containers A, B, C of equal volume contain oxygen, neon and methane respectively at same temperature and pressure. The increasing order of their masses is

(a) A < B < C

(b) B < C < A

(c) C < A < B

(d) C < B < A

2. A gas will approach ideal behaviour at

(a) Low temperature, low pressure

(b) Low temperature, high pressure

(c) High temperature, low pressure

(d) High temperature, high pressure

3. Containers A and B have same gas. Pressure, volume and temperature of A are all twice those of B. The ratio of number of molecules of A and B is

(a) 1 : 2

(b) 2 : 1

(c) 1 : 4

(d) 4 : 1

4. According to kinetic theory of gases,in an ideal gas,between two successive collisions a gas molecule travels

(a) In a circular path

(b) In a wavy path

(c) In a straight-line path

(d) With an accelerated velocity

5. When did substances exist in different crystalline forms the phenomenon is called:

(a) Allotropy

(b) Polymorphism

(c) Polymerization

(d) Isomorphism

6. Sl unit of pressure is:

(a) Pascal

(b) torr

(c) mm of Hg

(d) none of the above

7. If the pressure of a gas is increased then its mean free path becomes:

(a) 0

(b) Less

(c) More

(d) Infinity

8. 1 atmosphere is equal to:

(a) 1 torr

(b) 760 cm

(c) 760 mm

(d) 76 torr

9. Grahams law refers to:

(a) Boiling point of water

(b) Gaseous Diffusion

(c) Gas Compression

(d) Volume changes of gases

10. The rise or fall of a liquid within a tube of small bore is called:

(a) Surface Tension

(b) Capillary Action

(c) Viscosity

(d) Formation of Curvature

11. The rates of diffusion of gases are inversely proportional to square root of their densities. This statement refers to:

(a) Daltons Law

(b) Grahams Law

(c) Avogadros Law

(d) None of the Above

12. Cooling is caused by:

(a) Evaporation

(b) Convection

(c) Conduction

(d) none of the above

13. If helium and methane are allowed to diffuse out of the container under the similar conditions of temperature and pressure, then the ratio of rate of diffusion of helium to methane is:

(a) 2 : 1 (b) 1 : 2

(c) 3 : 5 (d) 4 : 1

14. Equal masses of ethane and hydrogen are mixed in an empty container at 25°C . The fraction of total pressure exerted by hydrogen is
    (a) 1 : 2
    (b) 1 : 1
    (c) 01 : 16
    (d) 15 : 16
15. The volume of 2.8 g of carbon monoxide at 27°C and 0.0821 atm is
    (a) 30 L
    (b) 3 L
    (c) 0.3 L
    (d) 1.5 L

Very Short:

1. What change in energy takes place when a molecule is formed from its atoms?
2. Arrange the following in order of increasing bond strengths.
3. Name the shapes of the following molecules: CH_4, C_2H_2, CO_2.
4. Arrange the following in order of increasing strengths of hydrogen bonding O, F, S, Cl, N
5. Identify the compound/compounds in the following in which S does not obey the Octet rule: SO_2, SF_2, SF_4, SF_6.
6. Name one compound each involving sp^3, sp^2, sp hybridization.
7. s-s, s-p, p-p form a bond, and only p-p form π bond.

Short Questions:

1. Which out of CH_3F and CH_3Cl has a higher dipole moment and why?
2. Define the term chemical bond. What are its different types?
3. Why covalent bonds are called directional bonds whereas ionic bonds are called non-directional?
4. AlF_3 is a high melting solid whereas SiF4 is a gas. Explain why?
5. Using the VSEPR theory identifies the type of hybridization and draw the structure of OF_2 What are oxidation states of O and F?
6. Account for the following: The experimentally determined N-F bond length in NF_3 is greater than the sum of the single covalent radii of N and F.

Long Questions:

1. State with reasons, which is more polar CO_2 or N_2O?
2. Out of peroxide ion (O_2) and superoxide ion (O_2) which has larger bond length and why?
3. Explain the formation of the following molecules according to the orbital concept, F_2, HF, O_2, H_2O, N_2, NH_3 molecules.
4. What is a hydrogen bond, what are its causes, and give the conditions for hydrogen bonding? What is the strength of hydrogen bonding? Describe the two types of hydrogen bonding.

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): Three states of matter are the result of balance between intermolecular forces and thermal energy of the molecules.

   Reason (R): Intermolecular forces tend to keep the molecules together but thermal energy of molecules tends to keep them apart.

   (i) Both A and R are true and R is the correct explanation of A.
   (ii) Both A and R are true but R is not the correct explanation of A.
   (iii) A is true but R is false.
   (iv) A is false but R is true.

2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): At constant temperature, pV vs V plot for real gases is not a straight line.

   Reason (R): At high pressure all gases have Z > 1 but at intermediate pressure most gases have Z < 1.

   (i) Both A and R are true and R is the correct explanation of A.
   (ii) Both A and R are true but R is not the correct explanation of A.
   (iii) A is true but R is false.
   (iv) A is false but R is true.

Case Study Based Question:

1. Intermolecular forces are the forces of attraction and repulsion that exist between molecules of a compound. These cause the compound to exist in a certain state of matter – solid, liquid or gas and affect the melting and boiling points of compounds as well as the solubilities of one substance in another. Attractive intermolecular forces are also called van der Waals' forces. These are weak forces.

   (1) Dipole-dipole forces act between the molecules possessing permanent dipole. Ends of dipoles possess 'partial charges'. The partial charge is:
   - (a) More than unit electronic charge
   - (b) Equal to unit electronic charge
   - (c) Less than unit electronic charge
   - (d) Double the unit electronic charge

   (2) The nature of inter-particle forces in benzene is:
   - (a) Dipole-dipole interaction
   - (b) Dispersion force
   - (c) Ion-dipole interaction
   - (d) H-bonding.

   (3) The interaction energy between two temporary dipoles is proportional to (where r is the distance between the two particles)
   - (a) $1/r^4$
   - (b) $1/r^2$
   - (c) $1/r^5$
   - (d) $1/r^6$

   (4) Attractive intermolecular forces known as van der Waals forces do not include which of the following types of interactions?
   - (a) London forces
   - (b) Dipole-dipole forces
   - (c) Ion-dipole forces
   - (d) Dipole-induced dipole forces

   (5) In which of the following molecules, the van der Waals forces are likely to be the most important in determining the m.pt. and b.pt?
   - (a) CO
   - (b) H_2S
   - (c) Br_2
   - (d) HCl

2. If a hydrogen atom is bonded to a highly electronegative element such as fluorine, oxygen, nitrogen, then the shared pair of electrons lies more towards the electronegative element. This leads to a polarity in the bond in such a way that a slight positive charge gets developed on H-atom, viz

   $H^{\delta+} : O^{\delta-}$ $\quad$ $H^{\delta+} : F^{\delta-}$ $\quad$ $H^{\delta+} : N^{\delta-}$

   Such a bond between the hydrogen atom of one molecule and the more electronegative atom of the same or another molecule is called a hydrogen bond.

   (1) Which of the following compounds can form hydrogen bond?
   - (a) CH_4
   - (b) H_2O
   - (c) NaCl
   - (d) $CHCl_3$

   (2) The boiling point is not affected due to hydrogen bonding in:
   - (a) Water
   - (b) Ammonia
   - (c) Methyl alcohol
   - (d) Hydrogen chloride

   (3) Unusual high b.p. of water is result of:
   - (a) Intermolecular hydrogen bonding
   - (b) Intramolecular hydrogen bonding
   - (c) Both intra and intermolecular hydrogen bonding
   - (d) High specific heat

   (4) Which of the following statements is not true?
   - (a) Intermolecular hydrogen bonds are formed between two different molecules of compounds.
   - (b) Intramolecular hydrogen bonds are formed between two different molecules of the same compound.
   - (c) Intramolecular hydrogen bonds are formed within the same molecule.
   - (d) Hydrogen bonds have a strong influence on the physical properties of a compound.

Answer Key

MCQ

1. (a) 0
2. (a) Sp^2
3. (b) Sp and sp^2
4. (c) sp^3, 0
5. (d) $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$
6. (c) Acetonitrile
7. (c) O_2^-
8. (c) Triangular
9. (b) $A_2 B_3$
10. (b) SF_4
11. (c) NaCl
12. (d) Ice
13. (d) NO^+ and CN^+
14. (c) HCl and He atoms
15. (b) sp and sp^2

Very Short Answer:

1. There is a fall in energy.
2. $F_2 < Cl_2 < O_2 < N_2$
3. CH_4: Tetrahedral; C_2H_2: Cylindrical; CO_2: linear
4. Cl < S < N < O <F.
5. SF_4, SF_6.
6. sp^3: CH_4: sp^2: C_2H_4: sp: C_2H_2
7. s-s, s-p, p-p form a bond, and only p-p form π bond.

Short Answer:

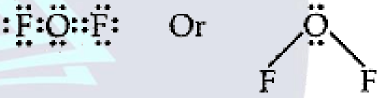
1. **Ans:** The dipole moment of CH_3Cl is greater than that of CH_3F. The C-F bond length in CH_3F is smaller than the C-Cl bond length in CH_3Cl. The charge separation in the C-F bond is more than in the Cl-C bond- fluoride being more electronegative than chlorine. The bond length has a greater effect than the charge separation. Hence the dipole moment of CH_3C1 is greater than that of CH_3F.

2. **Ans:** The attractive forces which hold the constituent atoms in molecules or species in lattices etc. are called a chemical bond. They are of the following types:
   1. Electrovalent or ionic bond
   2. Covalent bond
   3. Coordinate or dative bond
   4. metallic bond
   5. hydrogen bond
   6. van der Waals forces.

3. **Ans:** A covalent bond is formed by the overlap of half-filled atomic orbitals which have definite directions. Hence covalent bond is directional. In ionic compounds, each ion is surrounded by a number of oppositely charged ions and hence there is no definite direction.

4. **Ans:** AlF_3 is an ionic solid due to the large difference in electronegativities of Al and F whereas SiF_4 is a covalent compound and hence there are only weak van der Waal's forces among its molecules.

5. **Ans:** The electron dot structure of OF_2 is



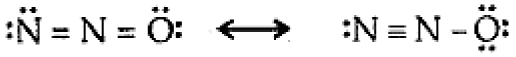
Thus, the central atom (O-atom) has 4 pairs of electrons (2 bond pairs and 2 lone pairs). Hence oxygen in OF_2 is sp^3 hybridized and the molecule is V-shaped oxidation state of F = – 1, oxidation state of O = + 2.

6. **Ans:** This is because both N and F are small and hence have high-electron density. So, they repel the bond pairs thereby making the N-F bond length larger.

Long Answer:

1. **Ans:** N_2O is more polar than CO_2 which is a linear molecule and thus symmetrical. Its net dipole moment is zero.

N_2O is linear but unsymmetrical. It is a resonance hybrid of the following canonical structures:



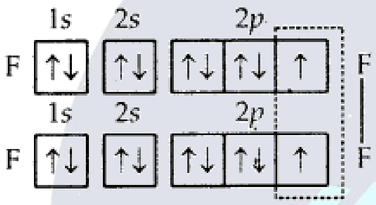
It has a net dipole moment of 0.116 D.

2. **Ans:** The bond order of O_2^- is 1.5 while that of O_2^{2-} is 1.0.

   The lesser the bond order, the greater is the bond length as the bond order is inversely proportional to bond length. (Hence O_2^{2-} has a larger bond length than O_2^{2-}.

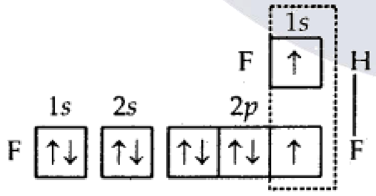
3. **Ans:**

   1. Formation of F_2 molecule. Atomic number (Z) of fluorine is 9 and its orbital electronic configuration is $1s^2\ 2s^2\ 2p^2x,\ 2p^2y,\ 2p^1z$. Thus, a fluorine atom has one half-filled atomic orbital. Therefore, two atoms of fluorine combine to form the fluorine molecule as a result of the combination for their half-filled atomic orbitals shown in Fig. The two atoms get linked by a single covalent bond

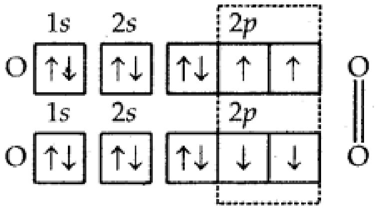


Formation of F_2 molecule

   2. Formation of HF molecule. Fluorine atom, as stated above, has one half-filled atomic orbital. Hydrogen atom (Z = 1) has only one electron in Is orbital. Thus, the hydrogen fluoride (HF) molecule. is formed as a result of the combination (or overlap) of the half-filled orbitals belonging to the participating atoms.



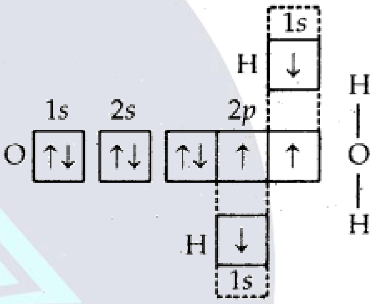
   3. Formation of O_2 molecules. The atomic number (Z) of oxygen is 8 and its orbital electronic configuration is $1s^2\ 2s^2\ 2p^2x\ 2p^1x\ 2p^1z$. This means that an oxygen atom has two half-filled orbitals with one electron each. Two such atoms will combine to form a molecule of oxygen as a result of the overlap of the half-filled orbitals with opposite spins of electrons.



Formation of O_2 molecule

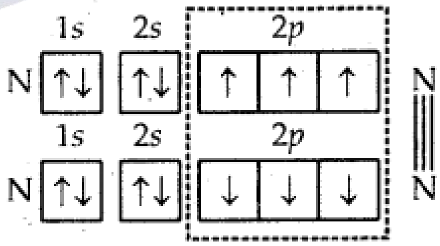
   Thus, the two atoms of oxygen are bonded to each other by two covalent bonds or double bonds (O = O).

   4. Formation of H_2O molecule. In the formation of the H_2O molecule, the two half-filled orbitals of the oxygen atom combine with the half-filled orbitals (1s) of the hydrogen atoms. Thus, the oxygen atom gets linked to the two hydrogen atoms by single covalent bonds as shown in



Formation of H_2O molecule

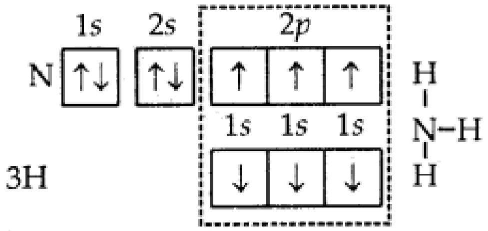
   5. Formation of N_2 molecule. The atomic number of nitrogen is 7 and its orbital electronic configuration is $1s^2\ 2s^2\ 2p^1x\ 2p^1y\ 2p^1\ z$. This shows that the nitrogen atom has three half-filled atomic orbitals. Two such atoms combine as a result of the overlap of the three half-filled orbitals and a triple bond gets formed (N = N)



Formation of N_2 molecule

   6. Formation of NH_3 molecule. In the formation of ammonia (NH_3) molecule, three half-filled orbitals present in the valence shell of nitrogen atom combine with 1s orbital of three hydrogen atoms with one electron

each. As a result, the nitrogen atom completes its octet and a molecule of NH_3 is formed in which the nitrogen atom is linked to three hydrogen atoms by covalent bonds.



Formation of NH_3 molecule

4. **Ans:** When hydrogen is connected to small highly electronegative atoms such as F, O, and N in such cases hydrogen forms an electrostatic weak bond with an electronegative atom of the second molecule, this type of bond binds the hydrogen atom of one molecule and the electronegative atom of the 2nd molecule is called as hydrogen bond. It is a weak bond and it is denoted by dotted lines e.g., in HF, hydrogen forms a weak bond with the electronegative F atom of the 2nd molecule neighboring HF.

$$\overset{\delta+}{H}-\overset{\delta-}{F}\ldots\ldots\overset{\delta+}{H}-\overset{\delta-}{F}\ldots\ldots\overset{\delta+}{H}-\overset{\delta-}{F}$$

So, it means hydrogen is acting as a bridge between two molecules by one covalent bond and the other by a hydrogen bond. Due to this hydrogen bonding, HF will not exist as a single molecule but it will exist as an associated molecule $(HF)n$. So hydrogen bond may be defined as a weak electrostatic bond that binds the hydrogen atom of one molecule and electronegative bond atoms (F, O, N) of the second neighboring molecule.

Cause of hydrogen bonding: When a hydrogen atom is bonded to an electronegative atom (say F, O, N) through a covalent bond, due to electronegativity difference, the electronegative atom attracts the shared pair of electrons towards its side with a great force as a result of which the shared pair of electrons will be displaced toward electronegative atom and away from a hydrogen atom.

Due to which hydrogen atom will acquire a slightly negative charge and if another molecule is brought nearer to it in such a way that electronegative atom of the second molecule faces hydrogen atom of the 1st molecule, due to opposite charges present on the atoms, an electrostatic bond will be formed between the hydrogen atom of one molecule and electronegative atom of 2nd molecule and this is called as hydrogen bond.

$$\overset{\delta+}{H}-\overset{\delta-}{F}\ldots\ldots\overset{\delta+}{H}-\overset{\delta-}{F}\ldots\ldots\overset{\delta+}{H}-\overset{\delta-}{F}$$

Conditions for hydrogen bonding. The following two necessary conditions for hydrogen bonding are:

1. Hydrogen atom should be connected to highly electronegative atom say F, O, or N.
2. The electronegative atom of which the hydrogen atom is connected should be the same in size.

   The smaller the size of the electronegative atom greater will be the attraction of that atom for shared pair of electrons and hence that pair will be displaced more nearer to that atom and hence that atom will develop greater negative charge and the hydrogen atom will develop a greater positive charge and hence hydrogen atom of this molecule will easily attract negative atom of the Ian molecule and hence a hydrogen bond will be easily formed.

   As both these conditions are satisfied only by F, O, N atoms so only three atoms show hydrogen bond.

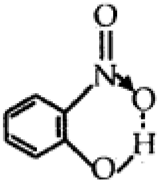
   Strength of Hydrogen Bond: A hydrogen bond is a very weak bond. It is weaker than an ionic or a covalent bond. Its strength ranges from 13 kJ mol-1 to 42 kJ mol^{-1}. The strength of the hydrogen bond for some of the molecules is the order H-F H (40 kJ mol-1) > O-H...... O (28 kJ mol^{-1}) > H-N...... H (13 kJ mol^{-1}) whereas the strength of a covalent bond is quite high. For example, the bond strength of the H-H bond in H_2 is 433 kJ mol^{-1}

Types of H-bonding

There are two types of hydrogen-bonds

1. Intermolecular hydrogen bond. It is formed between two different molecules of the same or different compounds. For example, H-bond in case of HF, alcohol, or water.
2. Intramolecular Hydrogen bond. It is formed when a hydrogen atom is in between the

two highly electronegative (F, O, N) atoms present within the same molecule. For example, in o-nitrophenol, hydrogen is in between the two oxygen atoms.



Assertion Reason Answer:

1. (i) Both A and R are true and R is the correct explanation of A.
2. (ii) Both A and R are true but R is not the correct explanation of A.

Case Study Answer:

1. Answer:

(1) (c) Less than unit electronic charge

(2) (b) Dispersion force

(3) (d) $1/r^6$

(4) (c) Ion-dipole forces

(5) (c) Br_2

2. Answer:

(1) (b) H_2O

(2) (d) Hydrogen chloride

(3) (a) Intermolecular hydrogen bonding

(4) (b) Intramolecular hydrogen bonds are formed between two different molecules of the same compound.

◆

Thermodynamics 6

Introduction

Chemical thermodynamics deals with the relationship between various form of energy in a process. Thermodynamics deals with macroscopic properties. This chapter introduces a major subsidiary thermodynamic property, the Gibbs free energy which lets us express the spontaneity of a process in terms of the properties of the system. This chapter helps to explain why gases expand or diffuse.

System and Surrounding

1. **System:** A specific portion of universe under study which is seperated from rest of the universe with a boundary is called system.
2. **Surroundings:** Rest of the universe which might be in a position to exchange energy and matter with the system is known as surrounding.

   ### Types of System:

   1. **Open system:** System can be open if it can exchange both energy and matter with surroundings.
   2. **Closed system:** System can be closed if it can exchange energy but not matter with surroundings.
   3. **Isolated system:** System can be isolated if it can neither exchange energy nor matter with surroundings.

Extensive Properties

The properties which depend upon mass of the substance is known as extensive properties i.e., mass, volume, internal energy, enthalpy etc.

Intensive Properties

The properties which are independent of mass of the substance is known as intensive properties i.e., temperature, pressure, density, refractive index.

Thermodynamic State of a System

A state is the condition of a system as specified by its physical properties. We can describe the state of a gas by quoting its pressure (p), volume (V), temperature (T), amount (n) etc. Variables like p, V, T are called state variables or state functions because their values depend only on the state of the system and not on how it is reached.

State Functions

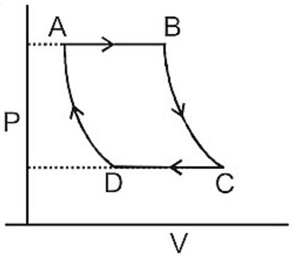
The thermodynamic parameters which depend only on initial and final states of system is known as state function. i.e., internal energy(E), Enthalpy (H), entropy (S), Gibb's free energy (G).

Path Functions: The thermodynamic parameters where value does not depend merely on initial and final state but depends upon the path followed is known as path function. i.e., heat (q), work done (W).

Thermodynamic Process: The sequence followed to change one thermodynamic state of a system into another is called thermodynamic process. The types of thermodynamic processes are:

1. **Isothermal process:** It is the process in which temperature is kept constant means temperature of initial and final state of system along with entire path of process is same.
2. **Isobaric process:** It is the process in which pressure is kept constant for entire process.
3. **Isochoric process:** It is the process in which volume is kept constant.
4. **Adiabatic process:** The process in which heat transaction across boundary is not allowed.
5. **Reversible process and Irreversible process:** In thermodynamics, a process is said to be reversible when energy change in each step of the process can be reversed by changing the variables such as pressure, volume or temperature acting on them. In such a process, the driving and opposing forces differ infinitesimally and the process can be reversed completely by increasing the opposing force by an infinitesimally small amount.

   Any process which does not take place in the above-mentioned manner is said to be an irreversible process. In an irreversible process the driving and opposing force differ by a large amount.



6. **Cyclic process:** It is the process which run in close loop means process in which initial and final states are identical.

Internal Energy

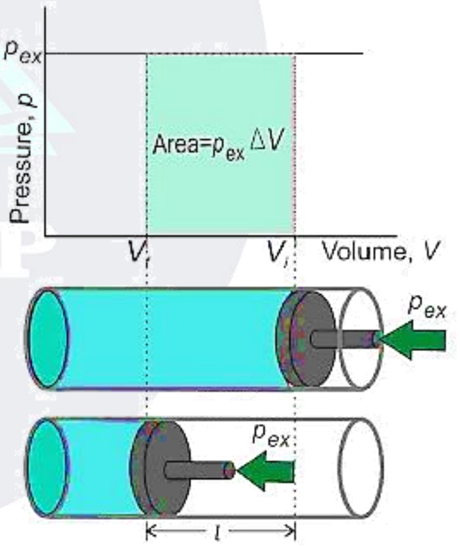
Every substance is associated with definite amount of energy that is called internal energy. It is an extensive property and a state function. Internal energy of ideal gases is a function of temperature only.

Pressure-Volume Work

It is the work done when the gas expands or contracts against the external pressure. Consider a cylinder containing one mole of an ideal gas fitted with a frictionless and weightless piston having an area of cross-section A. The total volume of the gas is Vi and the initial pressure of the gas inside P.

Let the external pressure acting on the piston is Pex. If the external pressure Pex is slightly greater than P piston moves downward till the pressure inside the cylinder becomes equal to Pex. Let this change be achieved in a single step and the final volume be Vf. During this compression, suppose the piston moves a very small distance Δl. Thus, the work done on the gas is given by,

$$\omega = -\int_{V_i}^{V_f} P_{ex} dv$$



Heat

The change in internal energy of a system can be brought about by the transfer of heat from the surroundings to the system or vice-versa. This exchange of energy between the system and surroundings is possible as a result of the temperature difference between them. This energy called heat is represented by Q.

First Law of Thermodynamics

First law of thermodynamics states the law of conservation of energy in a different manner. According to this law, whenever a quantity of one kind of energy disappears an equivalent amount of energy appears in some other form.

According to first law of thermodynamics,

$$\Delta U = q + W$$

Where, Q = Heat change

W = Work done

ΔU = Change in internal energy

Enthalpy (H)

The total heat content of a system at constant pressure is known as its enthalpy. Mathematically it is the sum of internal energy and pressure-volume energy

$$\Delta H = \Delta U + P\Delta V$$

It is an extensive property and a state function. Increase in enthalpy H is equal to heat absorbed at constant pressure.

Heat Capacity

Heat capacity is amount of heat require to raise the temperature of a system by unity. It is represented as "C". It is an extensive property and temperature dependent.

Types of heat capacity

1. Specific heat: For 1 gram system the heat loose or gained by system to bring one unit change in temperature is called specific heat denoted by 's'. specific heat is the intensive property.

$$S = \frac{C}{m}$$

2. Molar heat capacity: It is heat capacity for a system having 1 mole of material. It is represented as Cm. It is an intensive property.

$$C_m = \frac{C}{m}$$

3. Heat capacity at constant volume: Heat capacity of a system in isochoric condition is called heat capacity at constant volume, it is represented as C_v means molar heat capacity at constant volume.

$$C_v = \frac{dU}{dT}$$

4. Heat capacity at constant pressure: Heat capacity of a system in isobaric condition. It is represented by C_p means molar heat capacity at constant pressure.

$$C_p = \frac{dH}{dT}$$

Relation between Cp and Cv

We know that,

$$\Delta H = \Delta U + P\Delta V \qquad .....(i)$$

As per ideal gas equation

$$P\Delta V = R\Delta T \qquad .....(ii)$$

From (i) and (ii)

$$\Delta H = \Delta U + R\Delta T$$

$$\frac{\Delta H}{\Delta T} = \frac{\Delta U}{\Delta T} + R$$

$$C_p = C_v + R$$

$$C_p - C_v = R$$

Hess's Law

According to Hess's law, 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.

1st method: $C(s) + O_2(g) \rightarrow CO_2(g) = \Delta H$

2nd method: $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) = \Delta H_1$

$$CO(s) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) = \Delta H_2$$

According to Hess's law,

$$\Delta H = \Delta H_1 + \Delta H_2$$

Application of Hess's Law

1. Calculation of enthalpy of formation.
2. Determination of standard enthalpies of reactions.

Bond Dissociation Energy

The energy required to break one mole bond of a particular type in gaseous molecule is known as bond dissociation energy. For example, we consider the dissociation of water,

$$H - OH(g) \rightarrow H(g) + OH(g) = \Delta H \ = 498 \text{ kJ/mol}$$

Entropy

Entropy is a measure of degree of randomness or disorder in a system. Entropy is an extensive property and a state function. Its value depends upon the amount of substance present in the system.

Second Law of Thermodynamics

This states that the entropy of the universe always increases in every spontaneous (natural) change.

Free Energy (G)

Gibb's free energy is defined as,

$$\Delta G = \Delta H - T\Delta S$$

H is enthalpy, S is entropy and T is the temperature on Kelvin scale.

Measurement Of Change In Internal Energy and Enthalpy

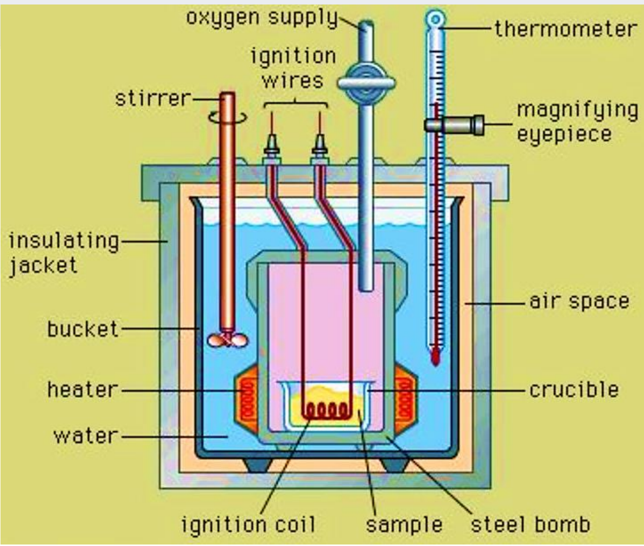
The experimental technique of measuring energy changes accompanying any chemical or physical process is called calorimetry.

These measurements are generally carried out under 2 conditions

1) at constant volume (ΔU or qv)

2) at constant pressure (ΔH or qp)

Measurements of ΔU



Internal energy change is measured experimentally using an apparatus called Bomb calorimeter.

It consists of a strong steel vessel which can stand high pressure. It is surrounded by a bigger vessel which contains water and is insulated. A thermometer and a stirrer are suspended in it.

Procedure

1) A known mass of compound is taken in the platinum cup. Oxygen under high pressure is introduced into the bomb. A current is passed through the filament immersed in the compound. Combustion of the compound takes place. The increase in the temperature of water is noted. From this, the heat capacity of the apparatus can be calculated.
2) The experiment is repeated as in step 1. As the reaction is carried out in a closed vessel, therefore, heat evolved is the heat of combustion at constant volume and hence is equal to internal energy change.

   The value of ΔU can be calculated using the formula

$$\Delta U = (Q \times \Delta t \times M) / m$$

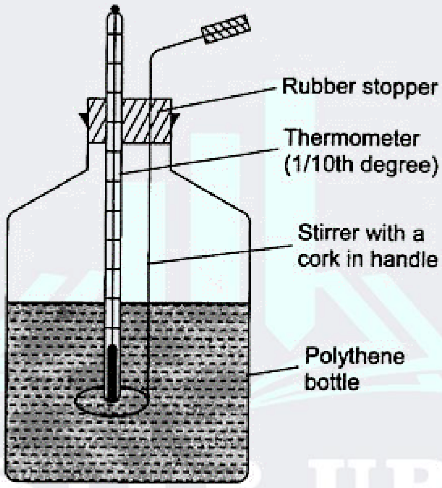
where Q =heat capacity of the calorimeter

Δt = rise in temperature

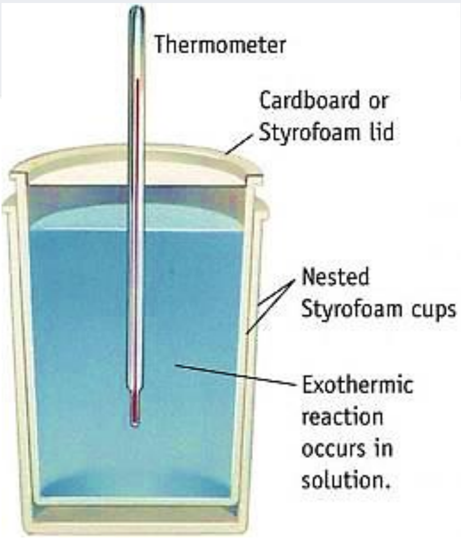
m= mass of the substance taken

M =molecular mass of the substance

Measurement of ΔH



Taking the example of heat of neutralisation of an acid with a base or vice versa, it can be determined using a simple calorimeter consisting of a polythene bottle fitted with a cork having two holes, one for the thermometer and the other for the stirrer.



Instead of polythene bottle, a foamed polystyrene cup with a cover is also sometimes used. It is called coffee cup calorimeter.

Taking the example of neutralisation of HCl with NaOH.

1) A known volume of HCL of known concentration ($100cm^3$ of 0.5 N) is taken in one beaker and an equal volume of NaOH of the same concentration ($100cm^3$ of 0.5 N) is taken in another beaker.
2) Both the beakers are kept in water bath till the solution attain the same temperature.
3) HCl solution kept in the first beaker is transferred into the polythene bottle. Immediately NaOH solution kept in the second beaker is added into the polythene bottle. Stirring is done to mix HCl and NaOH. The highest temperature attained is noted.

Suppose the initial temperature of the acid and the base = t_1 ° C

Final temperature of the solution after mixing = t_2 ° C

Rise in temperature= $(t_2 – t_1)$ °C

Total mass of the solution = 200 g

Heat produced = mass × specific heat × rise in temperature

Heat produced by neutralisation of 1000 cc of 1 N HCl

This give the heat of neutralisation per equivalent.

Heat of neutralisation of a strong acid by a strong base is always equal to 57.1 kJ equi-1 or 57.1 kJ mol-1 of H+ or OH– ions.

Measurement of ΔH or qp reaction for any reaction

For any reaction occurring in solution, the heat change accompanying the reaction at constant pressure i.e. enthalpy change can be measured by using the calorimeter.

The reaction is allowed to take place in the polythene bottle.

If the reaction is exothermic, temperature will rise and if the reaction is endothermic, temperature will fall.

For exothermic reaction, ΔH is negative whereas for endothermic reaction, ΔH is positive.

For the measurement of q_p or ΔH, the reaction may be carried out in a vessel with conducting walls.

This vessel may be placed in an insulated outer vessel containing water and fitted with a stirrer and a thermometer. The Rise or fall in temperature may be recorded and the result calculated.

Thermochemical Equation

When a balanced chemical equation not only indicates the quantities of the different reactants and products but also indicates the amount of heat evolved or absorbed, it is called thermochemical equation.

Fractional coefficients may be used in writing a thermochemical equation.

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(l)+285.8KJ\ mol^{-1}$$

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(l)\quad \Delta H=-285.8KJ\ mol^{-1}$$

285.8 KJ mol-1 of heat is produced when 1 mole of hydrogen reacts with 0.5 mole of Oxygen. If the quantities of reactants are doubled, the heat produced will also be doubled.

$$2H_2(g)+O_2(g)\longrightarrow 2H_2O(l)+571.6KJ\ mol^{-1}$$

$$2H_2(g)+O_2(g)\longrightarrow 2H_2O(l),\quad \Delta H=-571.6KJ\ mol^{-1}$$

Conventions about thermochemical equation

1) For exothermic reaction, ΔH is negative whereas for endothermic reaction, ΔH is positive.
2) ΔH values are for the standard state of the substance (298 K and 1 bar pressure)

3) The coefficients of different substances represent the number of moles reacted and formed for the heat change represented in the equation.

4) The physical state of the different substances must be mentioned as the heat evolved or absorbed depends upon the physical state.

5) If the coefficient of the substances is multiplied or divided by some number, the value of ΔH is multiplied or divide by the same number.

6) If the reaction is reversed, the sign of ΔH changes but the magnitude remains the same.

Heat of reaction or Enthalpy of reaction or Enthalpy change of reaction

The amount of heat evolved or absorbed in a chemical reaction when the number of moles of reactants as represented by the chemical equation have completely reacted, is called the heat of reaction or enthalpy of reaction or enthalpy change of reaction.

It is represented by Δr H.

For example

$$CH_4(g)+O_2(g)\longrightarrow CO_2(g)+2H_2O(l) \quad \Delta H=-890.4KJ\ mol^{-1}$$

$$C(s)+H_2O(g)\longrightarrow CO(g)+H_2(g) \quad \Delta H=131KJ\ mol^{-1}$$

1 mole of methane combines completely with 2 moles of Oxygen gas, 890.4 KJ of heat is produced.

1 mole of solid carbon react completely with one mole of steam ,131.4 KJ of heat is absorbed.

Enthalpy of reaction, ΔH = Sum of enthalpies of products – Sum of enthalpies of reactants

$\Delta H = \sum a_i H$ (products) – $\sum b_i H$ (reactants)

where symbol ∑ represent summation, ai and bi represents the coefficient of the products and reactants.

If the reaction is reversed, the sign of ΔH changes

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(l) \quad \Delta H=-285.8KJ\ mol^{-1}$$

$$H_2O(l)\longrightarrow H_2(g)+\frac{1}{2}O_2(g) \quad \Delta H=285.8KJ\ mol^{-1}$$

Factors on which the heat of reaction depends

1) Quantities of the reactants involved

If the quantities of reactants are doubled, the heat of reaction is also doubled.

2) Physical state of the reactants and products

The physical state of the reactants and products affects the heat of reaction.

When hydrogen and oxygen gas combine to form liquid water, the heat of reaction is different than when they combine to form water in the gaseous state.

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(l) \quad \Delta H=-285.8KJ\ mol^{-1}$$

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(g) \quad \Delta H=-241.8KJ\ mol^{-1}$$

It is essential to write the symbols s, l, g or aq to indicate whether a particular substance is a solid, liquid, gaseous or an aqueous solution.

3) Allotropic modification

For elements like Sulphur and carbon which exist in different allotropic modification, the heat of reaction is different in different allotropic form is involved in the reaction.

$$C(diamond) + O_2(g) \longrightarrow CO_2(g), \quad \Delta H = -395.4KJ\ mol^{-1}$$

$$C(graphite) + O_2(g) \longrightarrow CO_2(g), \quad \Delta H = -395.4KJ\ mol^{-1}$$

4) Concentration of solution

Heat changes occurs when a solute is dissolved in a solvent to form a solution or when solution is diluted.

Therefore, if the solutions are involved in a reaction, their concentration affect the heat of reaction.

5) Temperature

The heat of reaction depends upon the temperature at which the reactants and products are taken. The values are usually reported at 298 K.

6) Conditions of constant pressure or constant volume

Whether the reaction take place at constant pressure or at constant volume.

Standard enthalpy of reaction

The enthalpy change of a reaction depends upon the condition under which the reaction is carried out. Hence it is essential to specify some standard conditions.

The standard enthalpy of a reaction is the enthalpy change accompanying the reaction when all the reactants and products are taken in their standard state.

A substance is said to be in standard state when it is in the purest and most stable form at 1 bar pressure and the specified temperature.

This temperature is usually taken as to 298 K.

Standard state of pure ethanol at 298 k is pure liquid ethanol at 298 K and 1 bar pressure.

in terms of S.I. unit, 1 atm=101.325 KPa whereas 1 bar = 10^5 Pa .

The enthalpy change of a reaction in the standard state is represented by the symbol ΔH°

Bond Enthalpy

Bond energy is the amount of energy released when 1 mole of bonds are formed from the isolated atoms in the gaseous state or the amount of energy required to dissociate one mole of bonds present between the atoms in the gaseous molecules.

It is represented by $\Delta_b H$ or $\Delta_{bond} H$.

For diatomic molecules like H_2, O_2, N_2, Cl_2, HCl, HF etc. the bond energies are equal to their dissociation energies. These may also be called as their enthalpy of atomisation.

For polyatomic molecules, the bond energy of a particular bond is not the same when present in different types of compounds.

The bond energy of a particular type of bond is not same even in the same compound.

For Ex: In CH4 the bond energy for first, second, third and fourth C-H bonds are not equal: their values being 427, 439, 452 and 347 KJ mol-1

$$\Delta_a H^\circ = 427 + 439 + 452 + 347$$

$$\Delta_a H^\circ = 1665 \text{ KJ mol}^{-1}$$

To calculate bond energy, an average is taken.

$$\Delta C - H = 1665 / 4 = 416 \text{ KJ mol}^{-1}$$

Bond energy usually means bond dissociation energy. It is always taken as positive because it is the energy required and not the energy released. It is the energy for one mole of a particular type of bonds and not for 1 mole of the substance.

Bond dissociation energies are obtained at 0 K by spectroscopic method whereas bond enthalpy are calculated by considering combustions from heat capacities and pΔV terms.

Bond enthalpy helps to calculate the enthalpy of formation of atoms.

For polyatomic molecules, the bond enthalpy of a particular bond is found from the values of the enthalpies of formation.

Bond enthalpy of heteronuclear diatomic molecules can be obtained directly from the experiments or may be calculated from the bond enthalpies of homonuclear diatomic molecules.

Spontaneous and Non-spontaneous Process

A process which under some conditions may take place by itself or by initiation independent of the rate is called spontaneous process.

A process which can take place by itself or has an urge or tendency to take place is called spontaneous process.

A spontaneous process is simply a process which is feasible.

The rate of the process may vary from extremely slow to extremely fast.

Examples of processes which take place by themselves:

1) Dissolution of common salt in water
2) Evaporation of water in an open vessel
3) Flow of heat from hot end to cold end or from a hot body to a cold body
4) Flow of water down a hill
5) Combination of nitric oxide and oxygen to form Nitrogen dioxide

$$2NO(g)+O_2(g)\longrightarrow 2NO_2(g)$$

Examples of processes which take place on initiation

1) Lightning of candle involving burning of wax
2) Heating of calcium carbonates to give calcium oxide and carbon dioxide

$$CaCO_3(s)\longrightarrow CaO(s)+CO_2(g)$$

3) Combination of hydrogen and oxygen to form water when initiated by passing an electric spark

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(g)$$

A process which can neither take place by itself nor by initiation is called a non-spontaneous process.

For Example

1) Flow of water up a hill
2) Flow of heat from cold body to a hot body
3) Diffusion of gas from low pressure to a high pressure
4) Dissolution of sand in water

The force which is responsible for the spontaneity of a process is called a driving force

Nature of driving force

In order to acquire maximum stability, every system tends to have minimum energy.

Tendency for minimum energy

For example

1) A stone lying at height has a tendency to fall down so as to have minimum potential energy
2) Water flows down a hill to have minimum energy
3) A wound watch spring has tendency to unbind itself to decrease its energy to minimum
4) Heat flows from hot body to cold body so that heat content of the hot body becomes minimum

All the processes are spontaneous because they have tendency to acquire minimum energy.

Consider the following exothermic reaction, all of which are spontaneous:

1) $H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(l) \quad \Delta rH^o=-285.8KJ\ mol^{-1}$

2) $N_2(g)+3H_2(g)\longrightarrow 2NH_3(g) \quad \Delta rH^o=-92.2KJ\ mol^{-1}$

3) $C(s)+O_2(g)\longrightarrow CO_2(g) \quad \Delta rH^o=-285.8KJ\ mol^{-1}$

All these reactions are accompanied by evolution of heat. The heat content of the products is less than those of the reactants. These reactions are spontaneous because they are accompanied by decrease of energy.

A tendency to attain minimum energy i.e., a negative value of enthalpy change, might be responsible for a process or a reaction to be spontaneous or feasible.

limitation of the criteria for minimum energy

1) A number of reactions are known which are endothermic i.e., for which ΔH is positive but still they are spontaneous.

1) Evaporation of water or melting of ice

It takes place by absorption of heat from the surrounding.

$$H_2O(l)\longrightarrow H_2O(g) \quad \Delta_{vap}H^o=40.8KJ\ mol^{-1}$$

$$H_2O(s)\longrightarrow H_2O(l) \quad \Delta_{fus}H^o=6KJ\ mol^{-1}$$

2) Dissolution of salts like NH_4Cl , KCl

$$NH_4Cl(s)+aq\longrightarrow NH_{4^+}(aq)+Cl^-(aq) \quad \Delta_rH^o=15.1KJ\ mol^{-1}$$

3) Decomposition of calcium carbonate on heating

$$CaCO_3(s)\longrightarrow CaO(s)+CO_2(g) \quad \Delta_rH^o=177.8KJ\ mol^{-1}$$

4) Decomposition of N_2O_5 at room temperature

$$2N_2O_5(s)\longrightarrow 2NO_2(g)+O_2(g) \quad \Delta rH^o=219KJ\ mol^{-1}$$

5) Decomposition of mercuric oxide on heating

$$2HgO(s)\longrightarrow 2Hg(l)+O_2(g) \quad \Delta rH^o=90.8KJ\ mol^{-1}$$

2) A number of reactions are known for which ΔH is zero but still they are spontaneous

Reaction between acetic acid and ethyl alcohol

$$CH_3COOH(l)+C_2H_5OH(l)\longrightarrow CH_3COOC_2H_5(l)+H_2O(l)$$

2) Expansion of an ideal gas into vacuum

3) Even those reactions for which ΔH is negative, rarely proceed to completion even though ΔH remains negative throughout.

4) Reversible reactions also occur.

$$H_2(g)+I_2(g)\longrightarrow 2HI(g)$$

$$2HI(g)\longrightarrow H_2(g)+I_2(g)$$

The energy factor or enthalpy factor cannot be the sole criterion for predicting the spontaneity or the feasibility of a process.

Tendency for maximum randomness

Suppose the two gases are enclosed in bulbs A and B connected to each other by a tube and kept separated by a stopcock. If the stock cock is opened the two gases mix completely. The gases which were confined to bulbs A and B separately are no longer in order. A disorder has come in or the randomness of the system has increased.

A spontaneous process for which ΔH = 0 is the spreading of a drop of ink in a beaker filled with water.

Second factor which is responsible for the spontaneity of a process is the tendency to acquire maximum randomness.

For example:

1) Evaporation of water take place because the gaseous water molecules are more random than the liquid water molecules. The process is spontaneous because it is accompanied by increase of randomness. Melting of ice is a spontaneous process because liquid state is more random than the solid state.
2) Dissolution of Ammonium Chloride is spontaneous because in the solid, the ions are fixed but when they go into the aqueous solution, they are free to move about.
3) Decomposition of solid calcium carbonate is spontaneous because CO_2 produced is more random than the solid $CaCO_3$.
4) Decomposition of N_2O_5 is spontaneous because 2 moles of gaseous N_2O_5 give 5 moles of gaseous product.
5) Decomposition of solid Mercury oxide is spontaneous because the liquid Mercury and gaseous oxygen formed are more random than solid HgO.

The overall tendency for a process to occur depends upon the resultant of the following two tendencies:

1) Tendency for minimum energy
2) Tendency for maximum randomness

The resultant of the above 2 tendencies which gives the overall tendency for a process to occur is called the driving force of the process.

For example:

E represents the tendency for minimum energy

R represents the tendency for maximum randomness.

D represent the overall tendency

1) Evaporation of water

$$H_2O(l) \longrightarrow H_2O(g) \quad \Delta H = -44KJ\ mol^{-1}$$

E opposes (process being endothermic), R favours (because gas is more random than liquid). Since the process is known to be spontaneous hence R must be greater than E.

2) Dissolution of NH_4Cl in water

$$NH_4Cl(s) + aq \longrightarrow NH_{4^+}(aq) + Cl^-(aq) \quad \Delta H = 15.1KJ\ mol^{-1}$$

In this process E opposes and R favour. Here again, the spontaneity of the process is explained by suggesting that R > E.

Summary

1. **System:** A part of universe which is under investigation.
2. **Surroundings:** The rest of the universe which is not a part of the system.
3. **State of the system:** The conditions of existence of a system when its macroscopic properties have definite values.
4. **State functions:** The thermodynamic quantities which depend only on the initial and final state of the system.
5. **Energy:** Energy is exchanged between the system and the surroundings as heat if they are at different temperatures.
6. The properties of the system whose value is independent of the amount of substance are called intensive properties. e.g., temperature, pressure, viscosity, surface tension, dielectric constant, specific heat capacity.
7. The properties of the system whose value depends upon the amount of substance present in the system are called extensive properties. e.g., mass, volume, surface area, energy, enthalpy, entropy, free energy, heat capacity.

8. Work is also a mode of transference of energy between system and the surroundings. Work done by the system on the surroundings is given by pΔV.
9. **Internal energy (U):** The energy associated with the system at a particular condition of temperature and pressure.
10. **Enthalpy (H):** It is sum of internal energy and pressure-volume energy of the system at a particular temperature and pressure. It is also called heat content ($H = E + pV$).
11. **Hess's law:** The enthalpy change in a particular reaction is the same whether the reaction takes place in one step or in a number of steps.
12. **Bond enthalpy:** The average amount of energy required to break one mole of the bonds of a particular type in gaseous molecules.
13. **Entropy (S):** It is a measure of randomness or disorder of the system. Thus, the order is Gas > Liquid > Solid.

Class : 11th Chemistry
Chapter- 6: Thermodynamics

Thermodynamics

Enthalpy Change $\triangle_r H$ -Reaction Enthalpy

$\Delta_r H = \sum a_i H_{products} - \sum_i b_i H_{reactants}$

(a) Standard Enthalpy of reactions is the enthalpy change for a reaction when all the participating substances are in their standard states.

(b) Enthalpy changes during phase transformations: Standard enthalpy of fusion / molar enthalpy of fusion, $\Delta_{fus}H^\theta$ is the enthalpy change that accompanies melting of one mole of a solid substance in standard state. Standard enthalpy of vaporization or molar enthalpy of vaporization. $\Delta_{vap}H^\theta$ is the amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure.

(c) Standard molar enthalpy of formation $\Delta_f H^\theta$ is the standard enthalpy change for the formation of one mole of a compound from its elements in their most stable state of aggregation.

Measurement of ΔU and ΔH

In calorimetry, the process is carried out in a vessel called calorimeter, immersed in a known volume of a liquid.

(a) U measurements: The energy changes are measured at constant volume. No work is done.

(b) H measurements: In exothermic reaction, heat is evolved, so q_p and $_r$H will be negative. In endothermic reaction, heat is absorbed, so q_p and $_r$H will be positive.

Enthalpy of Solutions
is the enthalpy change when one mole of a substance dissolves in a specified amount of solvent.

Lattice Enthalpy
is the enthalpy change when one mole of an ionic compound dissociates into its ions in gaseous state

Enthalpy of atomization
$\Delta_a H^\theta$ is the enthalpy change on breaking one mole of bonds completely to obtain atoms in gas phase

Standard Enthalpy of combution
$\Delta_c H^\theta$ is the enthalpy change per mole of a substance when it undergoes combustion and all reactants and products are in standard state.

Heat Capacity
$q = C \times m \times \Delta T = C\Delta T$

Entropy
$\Delta S_{Total} = \Delta S_{systems} + \Delta S_{surroundings}$
$\Delta = \frac{q_{rev}}{T}$

Gibb's Energy
*$\Delta G = \Delta H - T\Delta S$
ΔG is <0, process is spontaneous.
* ΔG is >0, process is non-spontaneous

$\triangle rH^\circ$
Σ bond enthalpies reactants – Σ bond enthalpies products

$\triangle_r G_\theta = -RT \operatorname{Ink}$

Enthaply, H
ΔH is negative: Exothermic reactions. ΔH is positive: Endothermic reactions

A spontaneous process is an irreversible process which may be reversed by some external agency

Relationship between C_p and C_v For An Ideal Gas
$C_p - C_v = R$

Extensive Property
property which does not depend on the quantity or size of matter present in the system. Temperature density, pressure.

Applications

$\text{Work} = P_{ex}A.l = -P_{ex}(V_f - V_l) = \int_{V_i}^{V_f} P_{ex}\, dV$

Reversible Process: The process which can be reversed at any moment by an infinitesimal change.

Irreversible Process: Processes other than reversible process.

At constant temperature $W_{rev} = 2.303\, nRT \log \frac{V_t}{V_i}$

For adiabatic change, $q=0$, $\Delta U = W_{ad}$

Terms

- **Systems and surroundings: A system refers to that part of universe in which observations are made and remaining universe constitutes the surroundings.**
- **Types of System:**

1. Open System: There is exchange of energy and matter between system and surroundings.
2. Closed System: There is no exchange of matter but exchange of energy is possible.
3. Isolated System: There is no exchange of energy or matter between the system and surroundings.
4. State of system : is described by its measurable or macroscopic properties.
5. Internal Energy: as a state function: It is the sum of chemical, electrical, mechanical or any other type of energy.
6. (a) Work: Adiabatic process is in which there is no transfer of heat between system and surroundings.

(b) Heat is change in internal energy of a system by transfer of heat from the surroundings to the system or vice-versa without expenditure of work. q is positive: Heat is transferred from surroundings to system. q is negative: Heat is transferred from system to surroundings.
(c) General Case First law of Thermodynamics: ΔU = q+w the energy of an isolated system is constant.

Hess's Law of Constant Heat summation

If a reaction takes place in several steps then its standard reaction enthalpy is the sum of standard enthalpies of international reactions into which the overall reactions may be divided at the same temperature.

$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 \ldots\ldots\ldots$

$$\begin{tikzcd}
\boxed{A} \arrow[r, "\Delta_r H_1"] \arrow[d, "\Delta_r H_1"'] & \boxed{C} \\
\boxed{B} \arrow[r, "\Delta_r H_2"] & \boxed{D} \arrow[u, "\Delta_r H_3"']
\end{tikzcd}$$

Important Questions

Multiple Choice questions-

1. Hesss law is an application of

(a) 1st law of Thermodynamics

(b) 2nd law of Thermodynamics

(c) Entropy change

(d) ΔH = ΔU + PΔV.

2. 5 mole of an ideal gas expand isothermally and irreversibly from a pressure of 10 atm to 1 atm against a constant external pressure of 1 atm. Wirr at 300 K is:

(a) -15.921 kJ

(b) -11.224 kJ

(c) -110.83 kJ

(d) None of these

3. At absolute zero the entropy of a perfect crystal is zero. This statement corresponds to which law of thermodynamics?

(a) Zeroth Law

(b) First Law

(c) Second Law

(d) Third Law

4. Which of the following has the highest entropy?

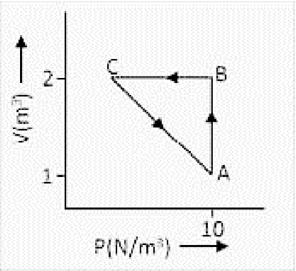
(a) Mercury

(b) Hydrogen

(c) Water

(d) Graphite

5. An ideal gas is taken through the cycle A → B → C → A as shown in figure. If the net heat supplied to the gas in cycle is 5 J, the work done by the gas in the process C → A.



(a) -5 J

(b) -15 J

(c) -10 J

(d) -20 J

6. One mole of which of the following has the highest entropy?

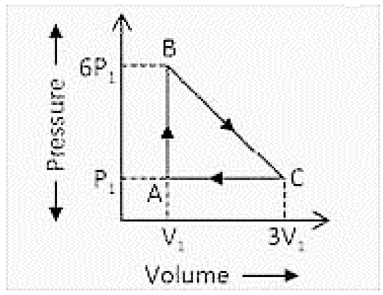
(a) Liquid Nitrogen

(b) Hydrogen Gas

(c) Mercury

(d) Diamond

7. An ideal gas is taken around the cycle ABCA as shown in P-V diagram The next work done by the gas during the cycle is equal to:



(a) $12P_1V_1$

(b) $6P_1V_1$

(c) $5P_1V_1$

(d) P_1V_1

8. Third law of thermodynamics provides a method to evaluate which property?

(a) Absolute Energy

(b) Absolute Enthalpy

(c) Absolute Entropy

(d) Absolute Free Energy

9. Which of the following is/are a reason that water is a desirable heat sink for use in calorimeters?

I) Waters heat specific capacity is very precisely known.

II) Water is readily available.

III) Water has an unusually large specific heat capacity.

(a) I only

(b) I and II

(c) I, II and III

(d) II only

10. In a chemical reaction the bond energy of reactants is more than the bond energy of the products. Therefore, the reaction is
    (a) Exothermic
    (b) Athermic
    (c) Endothermic
    (d) Endergonic
11. In a reversible process the system absorbs 600 kJ heat and performs 250 kJ work on the surroundings. What is the increase in the internal energy of the system?
    (a) 850 kJ
    (b) 600 kJ
    (c) 350 kJ
    (d) 250 kJ
12. Which of the following neutralization reactions is most exothermic?
    (a) HCl and NaOH
    (b) HCN and NaOH
    (c) HCl and NH4OH
    (d) CH3COOH and NH4OH
13. A student runs a reaction in a closed system. In the course of the reaction, 64.7 kJ of heat is released to the surroundings and 14.3 kJ of work is done on the system. What is the change in internal energy (ΔU) of the reaction?
    (a) -79.0 kJ
    (b) 50.4 kJ
    (c) 79.0 kJ
    (d) -50.4 kJ
14. Identify the correct statement from the following in a chemical reaction.
    (a) The entropy always increases
    (b) The change in entropy along with suitable change in enthalpy decides the fate of a reaction
    (c) The enthalpy always decreases
    (d) Both the enthalpy and the entropy remain constant
15. 2 mole of an ideal gas at 27° C expands isothermally and reversibly from a volume of 4 litters to 40 litre. The work done (in kJ) is:
    (a) $w = -28.72$ kJ
    (b) $w = -11.488$ kJ
    (c) $w = -5.736$ kJ
    (d) $w = -4.988$ kJ

Very Short:

1. Under what conditions the heat evolved or absorbed is equal to the internal energy change?
2. What is the sign of AH for endothermic reactions and why?
3. What is the relationship between the standard enthalpy of formation and the enthalpy of a compound?
4. Why enthalpy of neutralization of HF is greater than 57.1 kJ mol^{-1}?
5. What are the specific heat capacity and molar heat capacity for water?
6. Why enthalpy of neutralization is less if either the acid or the base or both are weak?
7. What do you mean by a system?

Short Questions:

1. Ice is lighter than water, but the entropy of ice is less than that of water. Explain.
2. Define spontaneity or-feasibility of a process.
3. Enthalpy of neutralization of CH_3COOH and NaOH is 55.9 kJ. What is the value of ΔH for ionization of CH_3COOH?
4. When 1 gm of liquid naphthalene (C10H8) solidifies, 150 J of heat is evolved. What is the enthalpy of fusion of $C_{10}H_8$?
5. Why most of the exothermic processes (reactions) are spontaneous?
6. What is meant by the term state function? Give examples.

Long Questions:

1. Define
    (i) Standard enthalpy of formation.
    (ii) Standard enthalpy of combustion
    (iii) Enthalpy of atomization
    (iv) Enthalpy of solution
    (v) Lattice enthalpy
    (vi) Thermochemical equation.
2. For the equilibrium $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ at 298 K, $K_c = 1.8 \times 10^{-7}$. What is $\Delta G°$ for the reaction? ($R = 8.314\ JK^{-1}\ mol^{-1}$).
3. Calculate the equilibrium constant, K, for the following reaction at 400 K?

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

Given that $\Delta_rH° = 80.0$ kJ mol^{-1} and $\Delta_rS° = 120$ JK^{-1} mol^{-1}.

4. Calculate the standard entropy change for the reaction X ⇌ Y if the value of $\Delta H^\circ = 28.40$ kJ and equilibrium constant is 1.8×10^{-7} at 298 K and $\Delta_r G^\circ = 38.484$ kJ.

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): Combustion of all organic compounds is an exothermic reaction.

   Reason (R): The enthalpies of all elements in their standard state are zero.

   (i) Both A and R are true and R is the correct explanation of A.

   (ii) Both A and R are true but R is not the correct explanation of A.

   (iii) A is true but R is false.

   (iv) A is false but R is true

2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): Spontaneous process is an irreversible process and may be reversed by some external agency.

   Reason (R): Decrease in enthalpy is a contributory factor for spontaneity.

   (i) Both A and R are true and R is the correct explanation of A.

   (ii) Both A and R are true but R is not the correct explanation of A.

   (iii) A is true but R is false.

   (iv) A is false but R is true.

Case Study Based Question:

1. This law was presented by Hess in 1840. According to the law, if a chemical reaction can be made to take place in a number of ways in one or in several steps, the total enthalpy change is always the same.

   Thus, the total enthalpy change of a chemical reaction depends on the initial and final stages only.

$$\begin{tikzcd}
A \arrow[r, "\Delta H_1"] & B \arrow[d, "\Delta H_2"] \\
D \arrow[u, "\Delta H_{\text{direct}}"] & C \arrow[l, "\Delta H_3"]
\end{tikzcd}$$

Total enthalpy changes from A to D,

$$\Delta H_{total} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$\Delta H_{total} + \Delta H_{direct} = 0$$

$$\text{i.e., } \Delta H_{total} = -\Delta H_{direct}$$

For example, formation of CO_2 from C in to different manners involves a total heat change of – 393.5 KJ/ mol

Single step process:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}; \quad \Delta H = -393.5 KJ/mol$$

Two-step process:

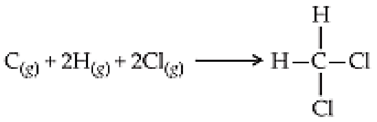
(i) $C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}; \quad \Delta H = -110.5 KJ/mol$

(ii) $CO(g) + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)}; \Delta H = -283.0 KJ/mol$

$$\Delta H_{Total} = -110.5 + (-283.0) = -393.5 KJ/mol$$

(1) In which of the enlisted cases, Hess's law is not applicable?
   (a) Determination of lattice energy
   (b) Determination of resonance energy
   (c) Determination of enthalpy of transformation of one allotropic form to another
   (d) Determination of entropy

(2) Use the bond energy data and calculate the enthalpy change for



$$C_{(g)} + 2H_{(g)} + 2Cl_{(g)} \longrightarrow H{-}\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}{-}Cl$$

The Bond energies of C – H and C – CI are 413 and 328 kJ mol^{-1} respectively.
   (a) – 1465 kJ/mol
   (b) 1465 kJ/mol
   (c) – 1482 kJ/mol
   (d) 1482 kJ/mol

(3) A hypothetical reaction, A 2B, proceeds through the following sequence of steps:

$$A \longrightarrow C; \quad \Delta H = q_1$$

$$C \longrightarrow D; \quad \Delta H = q_2$$

$$\frac{1}{2}D \longrightarrow B; \quad \Delta H = q_3$$

The heat of reaction is

(a) $q_1 - q_2 + 2q_3$

(b) $q_1 + q_2 - 2q_3$

(c) $q_1 + q_2 + 2q_3$

(d) $q_1 - 2q_2 + 2q_3$

2. The enthalpy of a system is defined as the sum of the internal energy of the system and the energy that arises due to its pressure and volume. Mathematically, the enthalpy is defined by the equation,

$$H = U + PV$$

Enthalpy change (ΔH) of a system is the heat absorbed or evolved by the system at constant pressure.

$$\Delta H = q_p,\ \Delta H = \Delta U + P\Delta V$$

(1) Which of the following is not correct about enthalpy?

(a) It is an extensive property

(b) It is not a state function

(c) Its absolute value cannot be determined

(d) Enthalpy of a compound is equal to the enthalpy of formation of that compound.

(2) Lattice enthalpies are determined by:

(a) Born-Haber cycle

(b) Hess's law

(c) lattice cycle

(d) None of these

(3) In which of the following thermochemical changes ΔH is always negative?

(a) Enthalpy of solution

(b) Enthalpy of hydrogenation

(c) Enthalpy of reaction

(d) Enthalpy of transition

Answer Key

MCQ

1. (d) 1st law of Thermodynamics
2. (b) -11.224 kJ
3. (d) Third Law
4. (b) Hydrogen
5. (a) -5 J
6. (b) Hydrogen Gas
7. (c) $5P_1V_1$
8. (c) Absolute Entropy
9. (c) I, II and III
10. (c) Endothermic
11. (c) 350 kJ
12. (a) HCl and NaOH
13. (d) -50.4 kJ
14. (b) The change in entropy along with suitable change in enthalpy decides the fate of a reaction
15. (b) w = -11.488 k

Very Short Answer:

1. At constant volume.
2. AH is positive as $\Delta H = H_p - H_r$ and $H_r < Hp$.
3. They are equal.
4. This is due to the high hydration energy of fluoride ions.
5. Specific heat capacity for H_2O = 4.18 $JK^{-1}\ g^{-1}$

   Molar heat capacity for H_2O = 4.18 × 18 = 75.24 $JK^{-1}\ mol^{-1}$.
6. A part of the heat is used up for dissociation of the weak acid or weak base or both
7. A specified part of the universe that is under thermodynamic observation is called a system.

Short Answer:

1. Ans: Water is the liquid form while ice is its solid form. Molecular motion in ice is restricted than in water, i.e., a disorder in ice is restricted than water, i.e., a disorder in ice is less than in water.

2. Ans: Spontaneity or feasibility of a process means its inherent tendency to occur on its own in a particular direction under a given set of conditions.

3. Ans: The heat of neutralization of strong acid and strong base + ΔH of ionization of CH_3COOH = Enthalpy of neutralization of CH_3COOH and NaOH

∴ – 57.1 kJ + ΔH of ionization of CH_3COOH = – 55.9 kJ

∴ ΔH of ionization of CH_3COOH

= (- 55.9 + 57.1) kJ

= 1.2 kJ.

4. **Ans:** Δ Hsolidifcation = – 150 × 128 = – 19200 J = – 19.2 kJ

[∵ M.wt. of $C_{10}H_8$ = 128]

5. **Ans:** ΔG = ΔH – TΔS; For exothermic reactions,

ΔH is -ve For a spontaneous process ΔG is to be -ve.

Thus, decrease in enthalpy (- AH) contributes significantly to the driving force (To make ΔG negative).

6. **Ans:** A state function is a thermodynamic property that depends upon the state of the system and is independent of the path followed to bring about the change. Internal energy change (ΔU), enthalpy change (ΔH) entropy change (ΔS), and free energy change (ΔG) are examples.

Long Answer:

1. **Ans: Standard enthalpy of formation:** The heat change accompanying the formation of 1 mole df a substance from its elements in their most stable state of aggregation is called its standard enthalpy of formation.

$H_2(g) + \frac{1}{2} O_2(g)\ H_2O(l)$; Δf He = 285.8 kJ mol^{-1}

(ii) **Standard enthalpy of combustion:** It is the heat change accompanying the complete combustion or burning of one mole of a substance in its standard state in excess of air or oxygen.

$C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(1)$;

ΔHθ = – 2658.0 kJ mol^{-1}.

(iii) **Enthalpy of atomization:** It is defined as the enthalpy change accompanying the breaking of one mole of a substance completely into its atoms in the gas phase.

$H_2(g) \rightarrow 2H(g)$ Δ_cHe = 435.0 kJ mol^{-1}

(iv) **Enthalpy of solution:** It is defined as the heat change when one mole of a substance dissolves in a specified amount of the solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving 2 moles of the substance in an infinite amount of the solvent.

(v) **Lattice Enthalpy:** The lattice enthalpy of an ionic compound is the enthalpy change that occurs when one mole of an ionic compound dissociates into its ions in a gaseous state.

$Na^+Cl^-(s) \longrightarrow Na^+(g) + Cl^-(g)$;

1 mole

$\Delta_{lattice}$ H^0 = +788 kJ mol^{-1}

(vi) **Thermochemical Equation:** A balanced chemical equation together with the value of its A^H is called a thermochemical equation.

$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$;

$\Delta_rH^0 = -1367$ kJ mol^{-1}

The above equation describes the combustion of liquid ethanol. The negative sign indicates that tills are an exothermic reaction. We specify the physical state along with the allotropic state of the substance in a thermochemical equation.

2. **Ans:**

$$K_P = K_C(RT)^{\Delta n}$$

$$\Delta n = n_p - n_r = 2 - 1 = 1.$$

T = 298 K, R= 8.314 JK^{-1} mol^{-1} (given)

$$\therefore\ K_P = 1.8\times10^{-7}\times8.314\times298 = 4.46\times10^{-4}$$

Now $\Delta_rG^0 = -2.303RT\log K_P$

$$= -2.303\times8.314\times298\times\log\left(4.46\times10^{-4}\right)$$

= 19111.86 J mol^{-1} = 19.12 KJ mol^{-1}.

3. **Ans:**

$$\Delta_rG^\circ = \Delta_rH^\circ - T\Delta_rS^\circ$$

$$= 80.0 - 400\times0.12 = 32.0kJ$$

$$\Delta_rG^\circ = -2.303RT\log K$$

$$32.0 = -2.303\times0.0831\times400\log K$$

or $\log K = -4.1782 = \bar{5}.8218$

or $K = -\text{Antilog}\ \bar{5}.8218 = 6.634\times10^{-5}$.

4. **Ans:**

$$\Delta_rG^\circ = -2.303RT\log K = 38484J\,(given)$$

$$\Delta_rG^0 = \Delta_rH^0 - T\Delta_rS^0$$

$$\Delta_rS^0 = \frac{\Delta_rH^0 - \Delta_rG^0}{T} = \frac{28400 - 38484}{298}$$

= −33.8 JK^{-1} mol^{-1}

Assertion Reason Answer:

1. (ii) Both A and R are true but R is not the correct explanation of A.
2. (ii) Both A and R are true but R is not the correct explanation of A.

Case Study Answer:

1. Answer:

(1) (d) Determination of entropy

(2) (c) – 1482 kJ/mol

(3) (c) $q_1 + q_2 + 2q_3$

2. Answer:

(1) (b) It is not a state function

(2) (a) Born-Haber cycle

(3) (b) Enthalpy of hydrogenation

◆ ◆

Equilibrium | 7

Introduction

Equilibrium is the most important characteristic property of reversible reactions. These reactions for which the forward reaction occurs to a much greater extent are considered to be unidirectional in nature and whenever the rate of forward reaction is equal to rate of backward reaction, equilibrium is attained, not to forget that equilibrium exists only in closed system.

It is the state of system at which temperature, pressure, volume and composition have fixed value and does not vary with time. Chemical Reactions can be divided into two categories:

Irreversible Reactions: The reactions which proceed to completion and the products fail to recombine to give back reactants. For example:

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$$

Reversible Reactions: The reactions which never go to completion and products recombine to give back reactants.
For example:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Physical Equilibrium

We know that solid, liquid and gas are the three states of substance. Therefore, three types of physical equilibrium are possible. These are:

$$\text{Solid(s)} \rightleftharpoons \text{liquid (l)}$$

$$\text{Liquid(l)} \rightleftharpoons \text{gas(g)}$$

$$\text{Solid(s)} \rightleftharpoons \text{gas(g)}$$

Here the sign double half arrows ($\rightleftharpoons$) pointing in the opposite directions is both for the reversible change as well as for the equilibrium state.

1. **Solid(s) – liquid(l) equilibrium:** At equilibrium two processes takes place at the same rate i.e.,

   Ice(s) $\rightleftharpoons$ water(l)

   $H_2O(s) \rightleftharpoons H_2O(l)$

   At equilibrium,
   Rate of melting of ice = Rate of freezing of water
   The temperature at which the solid and liquid states of a pure substance are in equilibrium at the atmospheric.
   pressure is called the normal freezing point or melting point of that substance.
2. Liquid(l) – gas(g) equilibrium:

   $$H_2O(l) \rightleftharpoons H_2O(g)$$

   In such type of equilibrium,
   Rate of vaporisation of water = Rate of condensation of water vapour

3. **Solid(s) – gas(g) equilibrium:** Such type of equilibrium is attained in case of volatile solids.

   Example: If solid iodine is placed in a closed vessel, violet vapours starts appearing in the vessel.

   The intensity of violet vapour increases with time and ultimately it becomes constant.

$$I_2(s) \rightleftharpoons I_2(g)$$

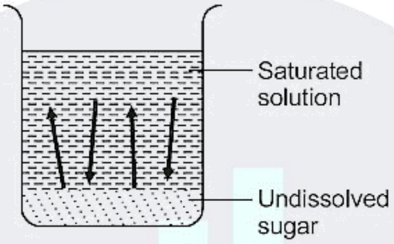
   In this equilibrium,

   Rate of sublimation = Rate of condensation

4. **Solids in liquids:** Suppose sugar is added continuously into a fixed volume of water at room temperature and stirred thoroughly with a glass rod. First the sugar will keep on dissolving but then a stage will come when no more sugar dissolves. Instead it settles down at the bottom. The solution is now said to be saturated and in a state of equilibrium. In this state

   Rate of dissolution = Rate of precipitation

$$\text{Sugar(s)} \rightleftharpoons \text{Sugar (in solution)}$$



   The amount of the solid in grams that dissolves in 100 g of the solvent to form a saturated solution at a particular temperature is called the solubility of that solid in the given solvent at that temperature.

Gases in liquids

Such type of equilibrium is present in soda water bottle in which CO_2 gas is dissolved in water under high pressure. There is a state of dynamic equilibrium between the CO_2 present in the solution and the vapours of the gas above the liquid surface at a given temperature.

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

Law of Mass Action

The rate at which a substance reacts is proportional to its active mass and hence the rate of a chemical reaction is proportional to the product of the active masses of the reactants.

The active mass means molar concentration i.e. number of moles dissolved per litre of the solution.

Suppose x g of NaOH are dissolved in V litres of solution.Then we can say:

Concentration of NaOH solution = x g in V litre = x/40 moles in V litres = $x / 40 \times V$ moles/Litre

Consider the reaction

$$A + B \text{ ————-> products}$$

According to Law of mass action,

Rate at which A reacts $\propto [A]$

Rate at which B reacts $\propto [B]$

Rate at which A and B react together $\propto [A]\,[B] = K\,[A]\,[B]$

where K is a constant of proportionality and is called velocity constant.

$$aA + bB \rightarrow \text{products}$$

$$\text{rate} \propto [A]^m\,[B]^n$$

The rate of a reaction is proportional to the product of the active masses of the reactants, each raised to the power equal to its stoichiometric coefficient as represented by the balanced chemical equation.

Henry's law

Periodic table may be defined as the tabular arrangement of elements in such a way that the elements having same properties are kept together.

$$m \propto p$$

$$m = kp$$

where k is Henry's constant and its value depends upon the nature of the gas, nature of liquid and temperature.

General Characteristics of Physical Equilibrium:

1. Equilibrium is possible only in a closed system at a given temperature.
2. Both the opposing processes occur at the same rate and there is a dynamic but stable condition.
3. All measurable properties of the system remain constant.
4. When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature.
5. The magnitude of such quantities at any stage indicates the extent to which the physical process has proceeded before reaching equilibrium.

Chemical Equilibrium

Every reversible reaction consists of one pair of reaction, one is forward and other is backward reaction. At one stage during reversible reactions, forward and backward reaction proceed at the same time with the same rate, the reaction is then said to be in equilibrium. If the opposing processes involve chemical reactions, the equilibrium is called Chemical equilibrium.

1. **Law of Chemical Equilibrium:** This law states that the rate of an elementary reaction is proportional to the product of the concentration of the reactants. At a constant temperature, the rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants each raised to a power equal to the corresponding stoichiometric coefficients as represented by the balanced chemical equation. Let us consider the reaction,

$$A + B \rightleftharpoons C + D$$

$r_f = K_f[A][B]$

$r_b = K_b[C][D]$

At equilibrium $r_f = r_b$.

$K_f[A][B] = K_b[C][D]$

$$K_c = \frac{K_c}{K_c} = \frac{[C][D]}{[A][B]}$$

Kc is called the equilibrium constant, [ ] ⟶ denotes active masses.

For a general reversible reaction,

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{[C]^c\,[D]^d}{[A]^A[B]^B}$$

2. **Equilibrium constant of reverse reaction:** Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.

$$K'^c = \frac{1}{K_c}$$

Relation between K_p and K_c

For a general reversible reaction

$aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C_C]^C[C_D]^d}{[C_A]^a[C_B]^b} \dots (1)$$

$$K_p = \frac{[P_C]^C[P_D]^d}{[P_A]^a[P_B]^b}$$

$$K_p = \frac{[C_C]^C \times [RT]^C . [C_D]^d \times [RT]^d}{[C_A]^a \times [RT]^a . [C_B]^b \times [RT]^b}$$

$$K_p = \frac{[C_C]^C[C_D]^d(RT)^{c+b}}{[C_A]^a[C_B]^b(RT)^{a+b}}$$

From Eq. (1),

$$K_p = K_C(RT)^{(c+d)-(a+b)}$$

$$K_p = K_c(RT)^{\Delta n}$$

Where, Δn = difference of stoichiometric coefficients of gaseous products and reactants.

3. **Characteristics of Equilibrium**
   i. At the state of equilibrium, certain available properties like pressure, concentration and density becomes constant.
   ii. Chemical equilibrium can be established from either side.
   iii. A catalyst can cause the state of equilibrium to be reached faster, but does not alter the state of equilibrium.
   iv. Chemical equilibrium is dynamic in nature.
   v. Any change in external stress (Pressure, temperature or concentration) causes disturbance in equilibrium state. The state of equilibrium being stable, is again reached by some adjustment.
   vi. If temperature is changed, a new equilibrium is achieved with a new value for relative concentration of products and reactants.
   vii. If temperature is kept constant, pressure and concentration of reactants / products is altered, system shifts in forward or backward direction in order to nullify the alteration (stress).

Factors Affecting Equilibria

i. **Change in Concentration:** When the concentration of any of the reactants or products in an equilibrium reaction is altered, the equilibrium mixture's composition changes in order to minimize the effect of the concentration change.

ii. **Change in Temperature:** According to Le-Chatelier's principle if the temperature of an equilibrium system is increased, the equilibrium will move in the direction of the added heat.

iii. **Change in Pressure:** The pressure has no effect on the equilibrium if the number of moles of gaseous reactants and products does not change. The change in pressure in both liquids and solids can be neglected in heterogeneous chemical equilibrium.

iv. **Change in Volume:** When the volume of a gaseous mixture at equilibrium is increased, the equilibrium moves in the direction of a larger number of gaseous molecules.

v. **Effect of a Catalyst:** The equilibrium is unaffected by the catalyst. This is due to the fact that the catalyst favours both forward and backward reactions equally.

Homogeneous Equilibria

When in an equilibrium reaction, all the reactants and the products are present in the same phase (i.e., gaseous or liquid) it is called a homogeneous equilibrium. For example,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Heterogeneous Equilibria

When in an equilibrium reaction, the reactants and the products are present in two or more than two phases, it is called a heterogeneous equilibrium.

The equilibrium between water vapour and liquid water in a closed container is an example of heterogeneous equilibrium.

$$H_2O(I) \rightleftharpoons H_2O(g)$$

Le Chatelier's Principle

It states that if a stress is applied to a system in equilibrium, the equilibrium for the time being gets disturbed. As a result system moves in a direction which tends to relieve the external stress and finally a new equilibrium is attained.

Ionic Equilibrium

Electrolyte: Electrolytes are the substances which conduct electricity in molten state or in solution. Example HCl, NaCl, KCl, CH_3COOH etc.

Arrhenius theory of Electrolytic dissociation: When an electrolyte is dissolved in a solvent it spontaneously dissociates into oppositely charged particles called ions, to a considerable extent. Electrolytic ionization or dissociation gives ions and unionized molecules in solution. For neutrality, the total charge on cations is equal to the total charge on the anions.

Degree of Dissociation (α): It is the fraction of one mole of the electrolyte that has dissociated under the given conditions. The value of α depends on temperature, dilution of electrolyte, nature of electrolyte and solvent.

α = No. of ionized moles/ Total mo. Moles

Ostwald's Law of Dilution:

According to this law, "The degree of ionization (or dissociation) of any weak electrolyte is inversely proportional to the square root of concentration."

$$\alpha = \sqrt{\frac{K}{C}}$$

Where, K = proportionality constant

Concepts of Acids and Bases

1. **Arrhenius Concept:**
    - **Acid:** Any substance when dissolved in water, increases the concentration of H+. e.g., HCl, H_2SO_4, HNO_3 etc.
    - **Base:** Any substance when dissolved in water, increases the concentration of OH-. e.g., NaOH, KOH etc.
2. **Bronsted - Lowry Concept:**
    - **Acid:** Species (Molecule or ion) that donates a proton to another species.
    - **Base:** Species (Molecule or ion) that accepts a proton from another species.

$$HCl(Acid) + NH_3(Base) \longrightarrow NH^+_4 + Cl^-$$

3. **Lewis acids and bases:**

According to Lewis concept of acids and bases, a Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor.

Lewis acids: H^+, Ag^+, Fe^{2+}, $AlCl^3$, BF^3, BCl^3, $BeCl^2$ etc.

Lewis Bases: Cl^-, CN^-, OH^-, X^-, NH^{-2}, SH^- etc.

An acid base reaction is the sharing of an electron pair with an acid by a base. This process is simply defined as coordination or neutralisation.

a. A strong acid is an acid that ionizes completely in water.

$$HCl(aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + Cl^-(aq)$$

b. A weak acid is an acid that is only partially ionized in water

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_2COO^-(aq) + H_3O^+(aq)$$

c. A strong base is a base that ionizes completely in water.

$$KOH(aq) \longrightarrow K^+(aq) + OH^-(aq)$$

d. A weak base is a base which is partially ionized in water

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH+4(aq) + OH^-(aq)$$

The pH Scale

pH of solution may be defined as negative logarithm of hydronium ion concentration.

$$pH = -\log [H_3O^+]$$

$$pH = \log \frac{1}{[H_3O^+]}$$

The pH range at 25°C is taken as 0 to 14.

pH = 7 Neutral

pH > 7 Basic

pH < 7 Acidic

Common Ion Effect

The suppression in the dissociation of a weak electrolyte by the addition of a strong electrolyte having a common ion is called common ion effect.

For example: Ionisation of acetic acid (CH_3COOH) and effect of addition of a small amount of acetate ion.

$$CH_3COOH(aq) \longrightarrow CH_3COO\text{-}(aq) + H\text{+}(aq)$$

$$CH_3COONa(aq) \longrightarrow CH_3COO\text{-}(aq) + Na\text{+}(aq)$$

Buffer Solution

A buffer solution is that solution which resists any change in its pH value on addition of small amount of acid or base. Although the pH of buffer changes on doing so, but the change in pH value will be less than the expected change. There are three types of buffer solution.

Acidic Buffer: This consists of solution of a weak acid and its salt with strong base. Example; CH_3COOH and CH_3COONa.

Basic Buffer: This consists of solution of weak base and its salt with strong acid. e.g., NH_4OH and NH_4Cl

Salt Buffer: It is a solution of salt which itself can act as a buffer. Such a salt is the salt of weak acid and weak base. For example,

$$CH_3COONH_4 \rightleftharpoons NH_4^+ + CH_3COO^-$$

When an acid is added, it reacts with CH_3COO^- to produce CH_3COOH and when a base is added, it react with NH^{4+} to produce NH_4OH.

Buffer Capacity

It is the number of moles of acid or base required by one litre of a buffer solution for changing its pH by one unit.

Buffer Capacity = No. of moles of acid or base adder per litre / Change in pH

Solubility and Solubility Product

The number of moles of solute in one litre of a saturated solution (mole / L) is defined as solubility. Let us calculate solubility of salt AgCl.

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

$K_{sp} = [Ag^+][Cl^-]$

Ksp is called solubility product.

In pure water,

$K_{sp} = [Ag^+][Cl^-]$

$K_{sp} = S_2$ $\{\because S = [Ag^+] = [Cl^-]\}$

$$S = \sqrt{K_{sp}}$$

Salt Hydrolysis

Salt hydrolysis is defined as the process in which a salt reacts with water to give back the acid and the base.

$$\text{Salt + water} \longrightarrow \text{Acid + Base}$$

$$BA + H_2O \longrightarrow HA + BOH$$

All salts are strong electrolytes and thus ionize completely in the aqueous solution.

(1) If the acid produced is strong and the base produced is weak.

$$B^+ + A^- + H_2O \longrightarrow H^+ + A^- + BOH$$

or

$$B^+ + H_2O \longrightarrow H^+ + BOH$$

In this case the cation reacts with water to give an acidic solution. This is called cationic hydrolysis.

(2) If the acid produced is weak and the base produced is strong.

$$B^+ + A^- + H_2O \longrightarrow HA + B^+ + OH^-$$

or

$$A^- + H_2O \longrightarrow HA + OH^-$$

In this case the anion reacts with water to give basic solution. This is called acidic hydrolysis.

Salt hydrolysis may be defined as the reaction of the cation or the anion of the salt with water to produce acidic or basic solution.

Depending upon the relative strength of the acid and the base produced, the resulting solution is acidic, basic or neutral.

(1) Salts of strong acid and strong base

$NaCl$, $NaNO_3$, Na_2SO_4, KCl, KNO_3 , K_2SO_4

$$NaCl + H_2O \longrightarrow NaOH + HCl$$

$$Na^+ + Cl^- + H_2O \longrightarrow Na^+ + OH^- + H^+ + Cl^-$$

$$H_2O \longrightarrow OH^- + H^+$$

It involves only ionization of water and no hydrolysis.So the solution is neutral.

The salts of strong acids and strong bases do not undergo hydrolysis and the resulting solution is neutral.

(2) Salts of weak acid and strong bases

CH_3COONa, Na_2CO_3, K_2CO_3, Na_3PO_4

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

$$CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$$

$$CH_3COO^- + H_2O \longrightarrow CH_3COOH + OH^-$$

As it produces OH^- ions, the solution of such a salt is alkaline in nature.

(3) Salts of strong acid and weak base

NH_4Cl , $CuSO_4$, NH_4NO_3 , $AlCl_3$, $CaCl_2$

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

$$NH4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

$$NH4^+ + H_2O \longrightarrow NH_4OH + H+$$

As it produces H+ ions, the solution of such a salt is acidic in nature.

(4) Salts of weak acid and weak base

CH_3COONH_4 , $AlPO_4$, $(NH_4)_2CO_3$

$$CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

It involves both anionic and cationic hydrolysis

Hydrolysis constant

Equation for the hydrolysis of a salt (BA) may be written as:

$$BA + H_2O \rightleftharpoons BOH + HA$$

$$B^+ + A^- + H_2O \rightleftharpoons BOH + H^+ + A^- or\ B^+ + H_2O \rightleftharpoons BOH + H^+$$

Hydrolysis constant, $K_h = \frac{[BOH][H^+]}{[B^+]}$

Degree of Hydrolysis

The degree of hydrolysis of a salt is defined as the function of the total salt which is hydrolyse i.e.

h = No. of moles of the salt hydrolysed / Total no. of moles the salt taken

Strengths of Acids and Bases

According to Arrhenius concept, an acid is defined as a substance which when dissolved in water gives H+ and a base is defined as a substance which when dissolved in water give OH^- ions.

Greater the number of H^+ ions produced in the aqueous solution, the stronger is the acid.

Greater the number of OH^- ions produced in the aqueous solution, the stronger is the base.

As greater is the dissociation constant of the weak acid (K_a), greater is the amount of H+ (aq) produced, therefore stronger is the acid.

K_a value gives a measure of the relative strength of the weak acid.

K_b value gives a measure of the relative strength of the weak base.

Suppose the weak acid is represented by HA. Suppose the initial concentration of HA is C mol/L and $\propto$ is the degree of dissociation.

$$HA + H_2O \rightleftharpoons H^+ (aq) + A^- (aq)$$

C 0 0 Initial conc

C (1-$\propto$)C$\propto$ C$\propto$ Conc at equilibrium

$$K_a = \frac{[H^+][A^-_{weak}]}{[HA_{weak}]}$$

where K_a is called dissociation constant of the acid.

$$K = \frac{Ca^2}{1-a}$$

If a is very samall 1- a ≈ 1 ⇒ $K_a = Ca^2$

$$\text{or} \quad a = \sqrt{\frac{K_a}{C}}$$

If two acids of equimolar concentration are taken

$$\frac{strength\ of\ the\ acid\ HA_1}{strength\ of\ the\ acid\ HA_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

The relative strength of two acids of equimolar concentration can be compared by taking square root of the ratios of their dissociation constants.

Ka, for CH_3COOH $= 1.8 \times 10^{-5}$

Ka for HCN $= 4.0 \times 10^{-10}$

$$\therefore \quad \frac{Strength\ of\ CH_3COOH}{Strength\ of\ HCN} = \sqrt{\frac{1.8\times10^{-5}}{4.0\times10^{-10}}}$$

$$= \sqrt{4.5\times10^{4}} = 2.1\times10^{2} = 210$$

CH_3COOH is nearly 192 times stronger than HCN.

The relative strength of two weak bases of equimolar concentration can be compared by taking square root of the ratios of their dissociation constants.

$$\frac{Strength\ of\ base(BOH)_1}{Strength\ of\ base(BOH)_2}=\sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

Where K_{b1} and K_{b2} are the dissociation constants of the two bases.

Since the ionization of an acid or a base increase with dilution, the strength of the acid or base increases with dilution.

K_a and K_b are taken as dimensionless quantities because the standard state concentration of all species involved is taken as mol L^{-1}

Polyprotic acid and polyacidic bases

Some acids like H_2SO_4, H_2CO_3, $(COOH)_2$, H_3PO_4, H_3AsO_4 contain more than one ionizable proton. Such acids are called polybasic or polyprotic acids. They ionize in steps.

$$H_2CO_3(aq)+H_2O(l)\rightleftharpoons H_3O^+(aq)+HCO_3^-(aq)$$

$$K_{a_1}=\frac{\left[H_3O^+\right]\left[HCO_3^-\right]}{\left[H_2CO_3\right]}=4.3\times10^{-7}$$

$$HCO_3^-(aq)+H_2O(l)\rightleftharpoons H_3O^+(aq)+CO_3^{2-}(aq)$$

$$K_{a_2}=\frac{\left[H_3O^+\right]\left[CO_3^{2-}\right]}{\left[HCO_3^-\right]}=5.6\times10^{-11}$$

$$H_3PO_4\rightleftharpoons H^++H_2PO_4^- \qquad K_1=7.5\times10^{-3} \qquad pK_1=2.12$$

$$H_2PO_4^-\rightleftharpoons H^++HPO_4^{-2} \qquad K_2=6.2\times10^{-8} \qquad pK_2=7.21$$

$$HPO_4^{-2}\rightleftharpoons H^++PO_4^{-3} \qquad K_3=4.8\times10^{-13} \qquad pK_3=12.30$$

$$H2A\,(aq)\rightleftharpoons H^+(aq)+HA^-(aq)$$

$$HA^-(aq)\rightleftharpoons H^+(aq)+A^{2-}(aq)$$

$$K_{a1}=\frac{[HA^1][H^+]}{[H_2A]}$$

$$K_{a2}=\frac{[A^{2-}][H^+]}{[HA^-]}$$

$K_a = K_{a1}\times K_{a2}$

For a tribasic acid , the overall ionization constant will be product of the ionization constant of the three steps i.e.

$K_a = K_{a1}\times K_{a2}\times K_{a3}$

$K_{a1} > K_{a2} > K_{a3}$

It is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces.

Greater the charge on the negative ion, more difficult it becomes to remove a proton.

According to Bronsted -Lowry concept, the relative strength of two acids is compared by comparing their tendencies to donate protons. The relative strength of two bases is compared by comparing their tendencies to accept proton.

The relative strength of the two acids or the two bases involved in the two acid-base conjugate pairs can be found out if we know whether forward reaction is favoured or backward reaction is favoured.

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

$acid_1$ $base_2$ $acid_2$ $base_1$

Acid- Base Titration using Indicator

Titration is the measurement of the volume of a solution of one reactant that is required to react completely with a measured amount of another reactant.

As both the reactants are taken in the form of solution and the titration is the measurement of volume of one solution that must be added to another solution till the reaction is complete, this method of quantitative analysis is called volumetric analysis.

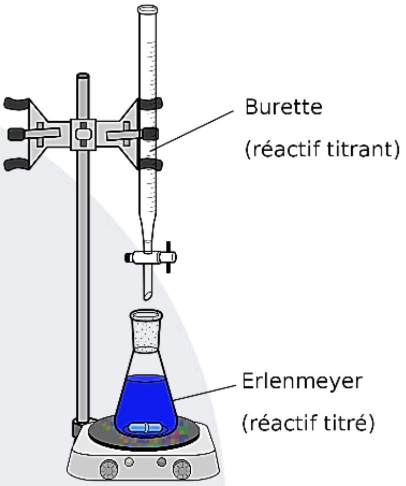
The concentration of the solution called as standard solution is known and it is desired to find the concentration of other by titration.

Apparatus of Titration

Procedure

1) A known volume of the solution is taken in the titration flask with the help of a pipette.
2) The other solution is taken in the burette which is graduated in cc's and has a stop cock at bottom to control the amount of flow into the flask.
3) The solution to be titrated is taken in the flask and is called titrate and the solution with which the titration is to be done that is taken in the burette is called the titrant.

   The point at which the required volume of one solution has been added to the other to exactly complete the reaction between the two is called end point or equivalence point.



Types of titrations

- Redox titrations involving oxidation and reduction.
- Acid -base titrations involving neutralization
- Precipitation titration
- Complexometric titration involving formation of complexes.

  The substance usually added into the solution taken in the titration flask to detect the equivalence point is called an indicator

Theory of acid base indicators

Acid base indicators are mostly complex organic molecules which are either weak acid or weak bases

For ex: Phenolphthalein is a weak organic acid (HPh) and methyl orange is a weak organic base (MeOH) .

Phenolphthalein and methyl orange dissociates in aqueous solution as :

$$HPh \rightleftharpoons H^+ + Ph^- \text{———————} (1)$$

colourless pink

$$MeOH \rightleftharpoons Me^+ + OH^- \text{———————} (2)$$

Yellow red colourless

The unionized form has one colour and the ions have different colour.

For Ex: HPh is colourless while Ph ions have pink colour. Similarly , MeOH has yellow colour while Me^+ have red colour.

As the medium changes from acidic to basic or vice versa, the equilibrium shifts either towards the right or towards the left and so the colour changes.

In acidic medium the equilibrium 1 is towards left and the solution is colourless while in the basic medium, OH^- ions will combine with the H^+ to form unionized water molecules, the equilibrium shifts towards the right and the solution has a pink colour.

In methyl orange in basic medium the equilibrium 2 is towards left and the colour is yellow while in the acidic medium H^+ ions combine with the OH^- ions and the equilibrium 2 shifts towards the right and the colour is red.

Phenolphthalein cannot be used as an indicator if the base is weak because the OH^- ions produced from the weak base are insufficient to shift the equilibrium 1 towards the right.

Methyl orange is not a suitable indicator if the acid is weak because the H^+ ions produced are insufficient to combine with OH^- ions and shift the equilibrium 2 towards the right.

pH at the end point of acid – base Titration

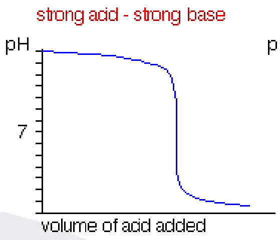
(1) If strong acid has been titrated with strong base, the pH at the end point is 7.

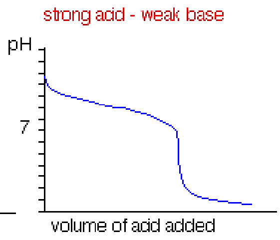
(2) If a weak acid or a weak base is involved in the titration, pH at the end point depends upon the hydrolysis of salt formed. In any type of acid-base titration, it is found that there is a sudden change in the pH value at the end.

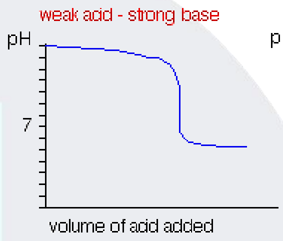
As the titration proceeds, if the pH values of the solution are measured or calculated theoretically and then plotted against the volume of the solution added, the curve obtained is called titration curve.

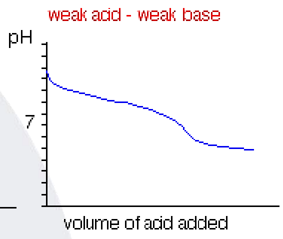
Titration Curve

The point at which there is sudden change in pH when a very small amount of titrant is added to the titrate is called point of inflection.









The steepness of the slope around the equivalence point is quite large in case of titration of strong acid against strong base whereas it is less steep if the acid or base is weak.

Large steepness means large change in pH on adding a very small volume of the solution. It may be pointed out that if a weak acid is titrated against a weak base, the change in pH at the end is so small that it is difficult to determine the end.

Selection of a Suitable Indicator

The indicator used should be such that it shows change in colour in the same pH range as required around the equivalence point.

Indicator	pH Range	Acid	Base
Thymol Blue	1.2 – 2.8	Red	Yellow
2, 4-Dinitrophenol	2.4 – 4.0	Colorless	Yellow
Methyl yellow	2.9 – 4.0	red	Yellow
Methyl orange	3.1 – 4.4	Red	Orange
Bromphenol blue	3.0 – 4.6	Yellow	Blue-violet
Methyl red	4.4 – 6.2	Red	yellow
p-Nitrophenol	5.0 – 7.0	Colorless	Yellow
Phenol red	6.4 – 8.0	Yellow	Red
Thymol blue	8.0 – 9.6	Yellow	Blue
Phenolphthalein	8.0 – 10.0	Colorless	Red
Alizarin yellow	10.0 – 12.0	Yellow	lilac
Salicyl yellow	10.0 – 12.0	Yellow	Orange-brown
Trinitrobenzoic acid	12.0 – 13.4	Colorless	Orange-red

(1) For titration of a strong acid against a strong base, any indicator out of methyl orange, methyl red, phenolphthalein or bromothymol blue can be used to determine the endpoint.

(2) For titration of weak acid like acetic Acid against a strong base, only phenolphthalein is a suitable indicator.

(3) For titration of weak base against strong acid, methyl orange or methyl red or bromothymol blue can be used as an indicator.

(4) For titration of weak acid with weak base, no indicator is found to function satisfactorily.

Colour change pKindicator =pH at the equivalence point

Consider an indicator which is a weak organic acid. Let it be represented by HIn. In aqueous solution, it dissociates as:

$$H_{In}\,(aq) \rightleftharpoons H^+\,(aq) + In^-\,(aq)$$

HIn and In⁻ have different colours.The equilibrium constant for the above reaction is :

$$K_{in} = [H+]\,[In^-]\;/\;[HIn]$$

The exact point of colour change will be at the pH when [HIn] = [In⁻]

$$K_{in} = -\log k_{In} = -\log\,[H^+]$$

For a particular titration, the indicator selected should be such for which pK_{In} = pH

Summary

1. **Equilibrium:** It represents the state of a process in which the properties like temperature, pressure, concentration of the system do not show any change with the passage of time.
2. **Physical equilibrium:** It is a state of equilibrium in which the two opposing processes involve changes in physical state only.
3. **Chemical equilibrium:** It is a state of equilibrium in which the two opposing processes involve change of chemical species.
4. **Reversible reaction:** A reversible reaction is one which proceeds in both the forward and backward directions.
5. **Law of mass action:** This law states that at constant temperature, the rate of chemical reaction is directly proportional to the product of molar concentrations of the reacting substances.
6. **Equilibrium constant (K):** It is the ratio of the product of the molar concentrations of the substances formed to that of the reacting substances raised to the powers equal to their stoichiometric coefficients in the chemical equation at a particular temperature.
7. **Henry's law:** The mass of a gas dissolved in a given mass of a solvent at any temperature is directly proportional to the pressure of the gas above the solvent.
8. **Le Chatelier's Principle:** When a system in dynamic equilibrium is subjected to a stress such as a change in concentration, pressure or temperature, the equilibrium shifts in a direction that opposes or reduces the stress.
9. **Strong electrolytes:** Electrolytes which are ionized almost completely in aqueous solution under similar conditions of concentration and temperature are called strong electrolytes.
10. **Weak electrolytes:** Electrolytes which are poorly ionized in aqueous solution under similar conditions of concentration and temperature are called weak electrolytes.
11. **Solubility product:** It is the product of concentration of ions in a saturated solution of a sparingly soluble salt at a given temperature.
12. **Arrhenius acid-base concept:** According to Arrhenious, an acid is a substance which gives hydrogen ions and base is a substance which gives hydroxyl ions in aqueous solutions.

13. **Bronsted-Lowry acid-base concept:** According to this concept, an acid is a proton donor and base is a proton acceptor.

14. **Lewis acid-bases concept:** According to this concept, an acid is an electron pair acceptor and base is an electron pair donor.

15. **pH value:** pH value of a solution is the negative logarithm of the hydrogen ion concentration (in moles per litre) present in it. Thus pH = $-\log[H^+]$

16. **Irreversible reaction:** If a reaction cannot take place in the reverse direction i.e., the products formed do not react to give back the reactants under the same conditions is called an irreversible reaction.

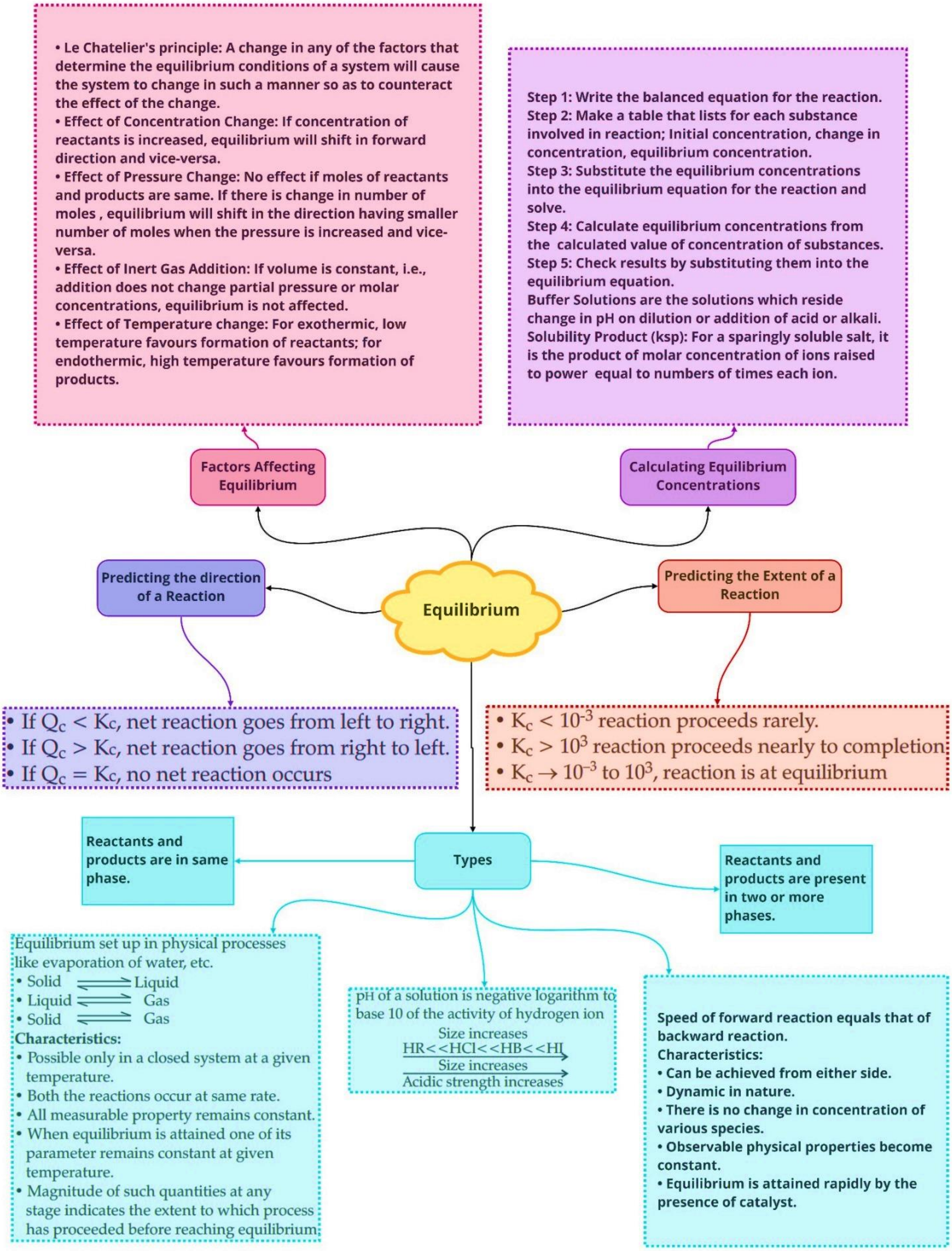
17. **Homogeneous equilibria:** When in an equilibrium reaction, all the reactants and the products are present in the same phase (i.e., gaseous or liquid), it is called a homogeneous equilibrium.

18. **Heterogeneous equilibrium:** When in an equilibrium reaction, the reactants and the products are present in two or more than two phases, it is called a heterogeneous equilibrium.

19. **Buffer solution:** It is defined as a solution which resists in its pH value even when small amounts of the acid or the base are added to it.

20. **Conjugate base:** A base formed by the loss of proton by an acid is called conjugate base of the acid.

Class : 11th Chemistry
Chapter- 7: Equilibrium (Part I)



Equilibrium

Factors Affecting Equilibrium

- **Le Chatelier's principle: 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 counteract the effect of the change.**
- **Effect of Concentration Change: If concentration of reactants is increased, equilibrium will shift in forward direction and vice-versa.**
- **Effect of Pressure Change: No effect if moles of reactants and products are same. If there is change in number of moles , equilibrium will shift in the direction having smaller number of moles when the pressure is increased and vice-versa.**
- **Effect of Inert Gas Addition: If volume is constant, i.e., addition does not change partial pressure or molar concentrations, equilibrium is not affected.**
- **Effect of Temperature change: For exothermic, low temperature favours formation of reactants; for endothermic, high temperature favours formation of products.**

Calculating Equilibrium Concentrations

Step 1: Write the balanced equation for the reaction.
Step 2: Make a table that lists for each substance involved in reaction; Initial concentration, change in concentration, equilibrium concentration.
Step 3: Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve.
Step 4: Calculate equilibrium concentrations from the calculated value of concentration of substances.
Step 5: Check results by substituting them into the equilibrium equation.
Buffer Solutions are the solutions which reside change in pH on dilution or addition of acid or alkali.
Solubility Product (ksp): For a sparingly soluble salt, it is the product of molar concentration of ions raised to power equal to numbers of times each ion.

Predicting the direction of a Reaction

- If $Q_c < K_c$, net reaction goes from left to right.
- If $Q_c > K_c$, net reaction goes from right to left.
- If $Q_c = K_c$, no net reaction occurs

Predicting the Extent of a Reaction

- $K_c < 10^{-3}$ reaction proceeds rarely.
- $K_c > 10^{3}$ reaction proceeds nearly to completion
- $K_c \rightarrow 10^{-3}$ to 10^{3}, reaction is at equilibrium

Types

Reactants and products are in same phase.

Reactants and products are present in two or more phases.

Equilibrium set up in physical processes like evaporation of water, etc.
- Solid $\rightleftharpoons$ Liquid
- Liquid $\rightleftharpoons$ Gas
- Solid $\rightleftharpoons$ Gas

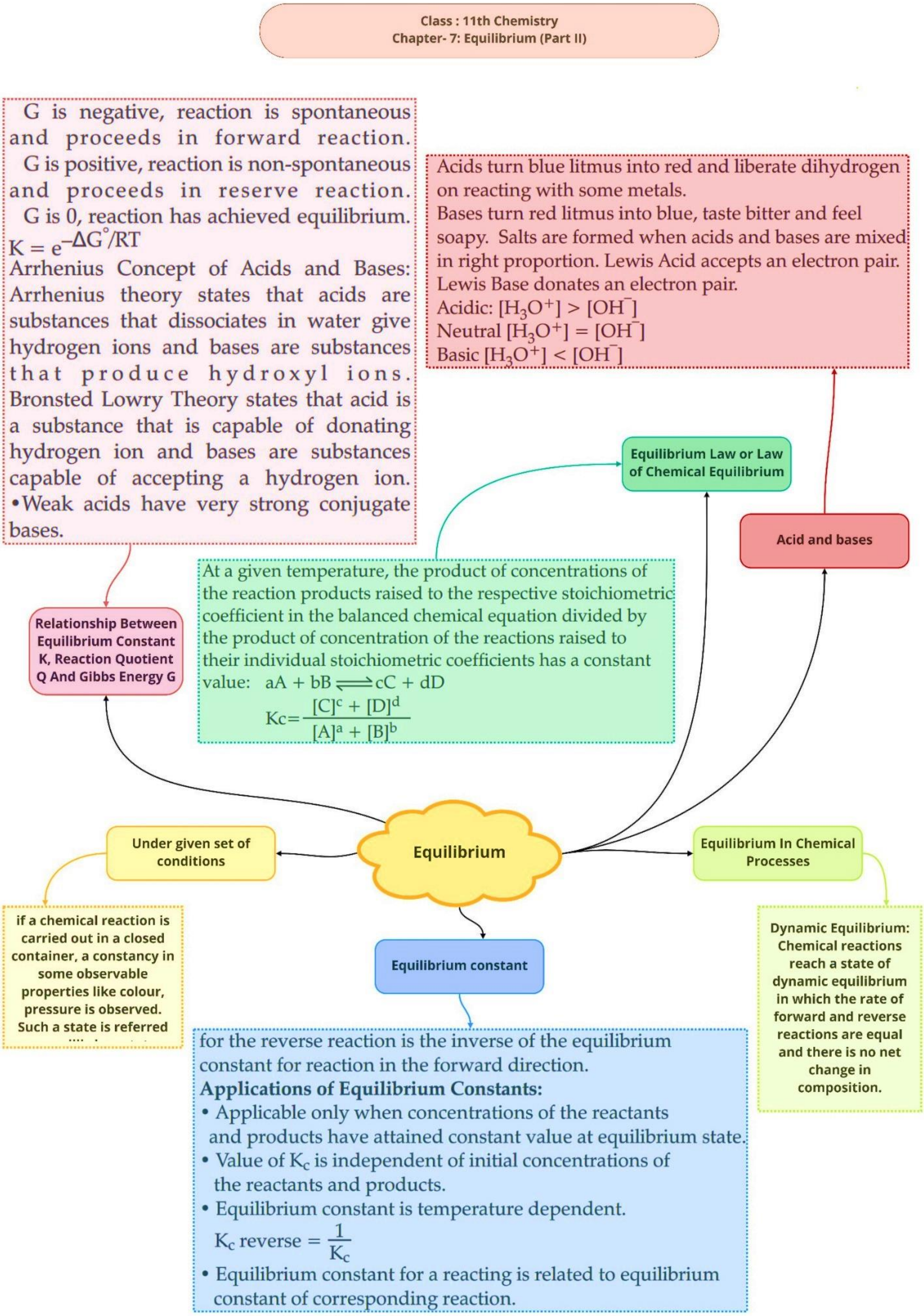
Characteristics:
- Possible only in a closed system at a given temperature.
- Both the reactions occur at same rate.
- All measurable property remains constant.
- When equilibrium is attained one of its parameter remains constant at given temperature.
- Magnitude of such quantities at any stage indicates the extent to which process has proceeded before reaching equilibrium

pH of a solution is negative logarithm to base 10 of the activity of hydrogen ion

$$\underset{\text{Acidic strength increases}}{\xrightarrow[\text{}]{\text{Size increases}}} \quad \overset{\text{Size increases}}{\underline{\text{HR<<HCl<<HB<<HI}}}$$

Speed of forward reaction equals that of backward reaction.
Characteristics:
- **Can be achieved from either side.**
- **Dynamic in nature.**
- **There is no change in concentration of various species.**
- **Observable physical properties become constant.**
- **Equilibrium is attained rapidly by the presence of catalyst.**

Class : 11th Chemistry
Chapter- 7: Equilibrium (Part II)



G is negative, reaction is spontaneous and proceeds in forward reaction. G is positive, reaction is non-spontaneous and proceeds in reserve reaction. G is 0, reaction has achieved equilibrium. $K = e^{-\Delta G^{\circ}/RT}$ Arrhenius Concept of Acids and Bases: Arrhenius theory states that acids are substances that dissociates in water give hydrogen ions and bases are substances that produce hydroxyl ions. Bronsted Lowry Theory states that acid is a substance that is capable of donating hydrogen ion and bases are substances capable of accepting a hydrogen ion.
- Weak acids have very strong conjugate bases.

Relationship Between Equilibrium Constant K, Reaction Quotient Q And Gibbs Energy G

Acids turn blue litmus into red and liberate dihydrogen on reacting with some metals.
Bases turn red litmus into blue, taste bitter and feel soapy. Salts are formed when acids and bases are mixed in right proportion. Lewis Acid accepts an electron pair. Lewis Base donates an electron pair.
Acidic: $[H_3O^+] > [OH^-]$
Neutral $[H_3O^+] = [OH^-]$
Basic $[H_3O^+] < [OH^-]$

Acid and bases

Equilibrium Law or 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 concentration of the reactions raised to their individual stoichiometric coefficients has a constant value: $aA + bB \rightleftharpoons cC + dD$

$$Kc = \frac{[C]^c + [D]^d}{[A]^a + [B]^b}$$

Equilibrium

Under given set of conditions

if a chemical reaction is carried out in a closed container, a constancy in some observable properties like colour, pressure is observed. Such a state is referred

Equilibrium constant

for the reverse reaction is the inverse of the equilibrium constant for reaction in the forward direction.

Applications of Equilibrium Constants:
- Applicable only when concentrations of the reactants and products have attained constant value at equilibrium state.
- Value of K_c is independent of initial concentrations of the reactants and products.
- Equilibrium constant is temperature dependent.

$$K_c \text{ reverse} = \frac{1}{K_c}$$

- Equilibrium constant for a reacting is related to equilibrium constant of corresponding reaction.

Equilibrium In Chemical Processes

Dynamic Equilibrium: Chemical reactions reach a state of dynamic equilibrium in which the rate of forward and reverse reactions are equal and there is no net change in composition.

Important Questions

Multiple Choice questions-

1. Which of the following fluoro-compounds is most likely to behave as a Lewis base?

(a) BF_3

(b) PF_3

(c) CF_4

(d) SiF_4

2. Calculate the pOH of a solution at 25°C that contains 1×10^{-10} M of hydronium ions, i.e. H_3O^+.

(a) 4.000

(b) 9.000

(c) 1.000

(d) 7.000

3. When two reactants, A and B are mixed to give products C and D, the reaction quotient, Q, at the initial stages of the reaction

(a) is zero

(b) Decreases With Time

(c) Is Independent of Time

(d) Increases With Time

4. 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is

(a) Not a buffer solution with pH < 7

(b) Not a buffer solution with pH > 7

(c) A buffer solution with pH < 7

(d) A buffer solution with pH > 7

5. If, in the reaction N_2O_4 $2NO_2$, x is that part of N_2O_4 which dissociates, then the number of molecules at equilibrium will be

(a) 1

(b) 3

(c) (1 + x)

(d) $(1 + xy)^2$

6. The solubility product of a salt having general formula MX_2. In water is: 4×10^{-12}. The concentration of M^{2+}ions in the aqueous solution of the salt is

(a) 4.0×10^{-10} M

(b) 1.6×10^{-4} M

(c) 1.0×10^{-4} M

(d) 2.0×10^{-6} M

7. Equimolar solutions of the following were prepared in water separately. Which one of the solutions will record the highest pH?

(a) $CaCl_2$

(b) $SrCl_2$

(c) $BaCl_2$

(d) $MgCl_2$

8. Oxidation number of Iodine varies from

(a) -1 to +1

(b) -1 to +7

(c) +3 to +5

(d) -1 to +5

9. Which of the following molecular species has unpaired electrons?

(a) N_2

(b) F_2

(c) O^{-}_{2}

(d) O_2^{-2}

10. A certain buffer solution contains equal concentration of X– and HX. The ka for HX is 10-8. The pH of the buffer is

(a) 3

(b) 8

(c) 11

(d) 14

11. Among the following the weakest Bronsted base is

(a) F–

(b) Cl–

(c) Br–

(d) I–

12. Which of the following statements is correct about the equilibrium constant?

(a) Its value increases by increase in temperature

(b) Its value decreases by decrease in temperature

(c) Its value may increase or decrease with increase in temperature

(d) Its value is constant at all temperatures

13. pH value of which one of the following is NOT equal to one.

    (a) 0.1 M CH_3COOH

    (b) 0.1 M HNO_3

    (c) 0.05 M H_2SO_4

    (d) 50cm^3 0.4 M HCl + 50cm^3 0.2 M NaOH

14. [OH−] in a solution is 1 mol L−. The pH the solution is

    (a) 1

    (b) 0

    (c) 14

    (d) 10^{-14}

15. What is the pH of a 0.10 M solution of barium hydroxide, $Ba(OH)_2$?

    (a) 11.31

    (b) 11.7

    (c) 13.30

    (d) None of these

Very Short:

1. Write the expression for the equilibrium constant K_p for the reaction

   $$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

2. How are Kc and Kp related to each other in the reaction

   $$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

3. What is the equilibrium constant expression for the reaction

   $$Al(s) + 3H^+(aq) \rightleftharpoons Al^{3+}(aq) + \frac{3}{2}H_2(g)$$

4. What happens to the equilibrium

   $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ if nitrogen is added to it

   (i) at constant volume

   (ii) at constant pressure?

5. What does the equilibrium K < I indicate?

6. For an exothermic reaction, what happens to the equilibrium constant if the temperature is increased?

7. Under what conditions, a reversible process becomes irreversible?

8. What is the effect of increasing pressure on the equilibrium?

   $$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)?$$

9. For which of the following cases does the reaction go farthest to completion: K = 1, K = 1010, K = 10-10.

10. Under what conditions ice water system is in equilibrium?

    (a) at 273 K

    (b) below 273 K

    (c) above 273 K.

Short Questions:

1. Justify the statement that water behaves like acid as well as a base on the basis of the protonic concept.

2. What is p^{OH}? What is its value for pure water at 298 K?

3. Calculate the p^H of a buffer solution containing 0.1 moles of acetic acid and 0.15 mole of sodium acetate. The ionization constant for acetic acid is 1.75×10^{-5}.

4. An aqueous solution of $CuSO_4$ is acidic while that of Na_2SO_4 is neutral. Explain.

5. The dissociation constants of HCN, CH_3COOH, and HF are 7.2×10^{-10}, 1.8×10^{-5}, and 6.7×10^{-4} respectively. Arrange them in increasing order of acid strength.

6. The dissociation of PCl_5 decreases in presence of Cl_2. Why?

Long Questions:

1. Explain chemical equilibrium with th^ help of an example of formation and decomposition of hydrogen iodide.

2. Name and explain the factors which influence the equilibrium state.

3. What is salt hydrolysis? Explain hydrolysis of salts of

   (i) strong acids and strong bases

   (ii) strong acids and weak bases

   (iii) strong bases and weak acids

   (iv) strong acids and weak bases.

4. Calculate the pH of $\frac{N}{1000}$ Sodium hydroxide solution assuming complete ionisation ($K_w = 1.0 \times 10^{-14}$).

5. Calculate the p^H of a 0.01 N solution of acetic acid. K_a for acetic acid is 1.8×10^{-5} at 25°C

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): Increasing order of acidity of hydrogen halides is HF < HCl < HBr < HI

   Reason (R): While comparing acids formed by the elements belonging to the same group of periodic tables, H–A bond strength is a more important factor in determining acidity of an acid than the polar nature of the bond.

   (i) Both A and R are true and R is the correct explanation of A.
   (ii) Both A and R are true but R is not the correct explanation of A.
   (iii) A is true but R is false.
   (iv) Both A and R are false.

2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): A solution containing a mixture of acetic acid and sodium acetate maintains a constant value of pH on addition of small amounts of acid or alkali.

   Reason (R): A solution containing a mixture of acetic acid and sodium acetate acts as a buffer solution around pH 4.75.

   (i) Both A and R are true and R is correct explanation of A.
   (ii) Both A and R are true but R is not the correct explanation of A.
   (iii) A is true but R is false.
   (iv) Both A and R are false.

Case Study Based Question:

1. Le Chatelier's principle is also known as the equilibrium law, used to predict the effect of change on a system at chemical equilibrium. This principle states that equilibrium adjusts the forward and backward reactions in such a way as to accept the change affecting the equilibrium condition. When factor-like concentration, pressure, temperature, inert gas that affect equilibrium are changed, the equilibrium will shift in that direction where the effects caused by these changes are nullified. This principle is also used to manipulate reversible reactions in order to obtain suitable outcomes.

(1) Which one of the following conditions will favour the maximum formation of the product in the reaction?

$$A_{2(g)} + B_{2(g)} \rightleftharpoons X_{2(g)}, \quad \Delta_r H = -X\,kJ\,?$$

(a) Low temperature and high pressure
(b) Low temperature and low pressure
(c) High temperature and high pressure
(d) High temperature and low pressure

(2) For the reversible reaction,

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + heat$$

The equilibrium shifts in forwarding direction

(a) By increasing the concentration of $NH_3(g)$
(b) By decreasing the pressure
(c) By decreasing the concentrations of $N_2(g)$ and $H_2(g)$
(d) By increasing pressure and decreasing temperature

(3) Favourable conditions for manufacture of ammonia by the reaction,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3; \quad \Delta H = -21.9\,kcal$$

(a) Low temperature, low pressure and catalyst
(b) Low temperature, high pressure and catalyst
(c) High temperature, low pressure and catalyst
(d) High temperature, high pressure and catalyst

(4) For the above equilibrium, the reactant concentration is doubled, what would happen then to equilibrium constant?

$$X + Y \rightleftharpoons P + Q$$

(a) Remains constant
(b) Be doubled
(c) Be halved
(d) Cannot be predicted

(5) In which one of the following equilibria will the point of equilibrium shift to left when the pressure of the system is increased?

(a) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

(b) $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$

(c) $C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$

(d) $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$

Answer Key

MCQ

1. (b) PF_3
2. (a) 4000
3. (d) Increases With Time
4. (a) Not a buffer solution with pH < 7
5. (a) 1
6. (c) 1.0×10^{-4} M
7. (c) $BaCl_2$
8. (b) -1 to +7
9. (c) $O^{-}{}_{2}$
10. (b) 8
11. (d) l^{-}
12. (c) Its value may increase or decrease with increase in temperature
13. (a) 0.1 M CH_3COOH
14. (c) 14
15. (c) 13.30

Very Short Answer:

1. $K_p = \frac{p_{H_2}^4}{p_{H_2O}^4} = \frac{p_{H_2}}{p_{H_2O}}$
2. $K_p = K_c$.
3. Kc = $[Al^{3+} (aq)][H2\ (g)^{3/2}/[H+\ (aq)]^3$.
4. The state of equilibrium remains unaffected.

   (ii) Dissociation increases, i.e., the equilibrium shifts forward.
5. The reaction does not proceed much in the forward direction.
6. K = K/K_b.

   K_b increases much more than when the temperature is increased in an exothermic reaction. Hence K decreases.
7. If one of the products (gaseous) is allowed to escape out (i.e., in the open vessel).
8. Equilibrium will shift in the forward direction forming more ammonia
9. The reaction having K = 1010 will go farthest to completion because the ratio (product)/(reactants) is maximum in this case.
10. (a) At 273 K.

Short Answer:

1. **Ans:** Water ionizes as $H_2O + H_2O \rightleftharpoons H_3O+ + OH–$

   With strong acids, water behaves as a base by accepting a proton from an acid.

   $HCl + H_2O \rightleftharpoons H_3O+\ (aq) + Cl–\ (aq)$

   While with bases, water behaves as an acid by liberating a proton

   $NH_3 + H_2O \rightleftharpoons NH_4+\ (aq) + OH\ (aq)$.

2. **Ans:** p^{OH} = – log [OH–]

   pH + p^{OH} = 14 for pure water at 298 K

   pH = 7

   or

   p^{OH} of water at 298 = 7.

3. **Ans:**

   $$p^H = p^{K_a} + \log\frac{[Salt]}{[Acid]}$$

   $$= -\log 1.75\times10^{-5} + \log\frac{0.15}{0.10}\left[p^{K_a} = -\log K_a\right]$$

   $$= -\log 1.75\times10^{-5} + \log 1.5 = 4.9.$$

4. **Ans:** $CuSO_4 + 2H_2O \rightleftharpoons Cu\ (OH)_2 + H_2SO_4$ (weak base strong acid)

   $CuSO_4$ is the salt of weak base Cu $(OH)_2$ and a strong acid H_2SO_4.

Thus, the solution will have free H^+ ions and will, therefore, be acidic.

Na_2SO_4, being the salt of a strong acid H_2SO_4 and a strong base.

NaOH does not undergo hydrolysis. The solution is, therefore, neutral.

5. **Ans:** More the value of Ka, the stronger the acid

Their Ka1S are

$$6.7 \times 10^{-4} > 1.8 \times 10^{-5} > 7.2 \times 10^{-10}$$

$\therefore$ HCN < CH_3COOH < HF.

6. **Ans:** For $PCl_5 \rightleftharpoons PCl_3 + Cl_2$.

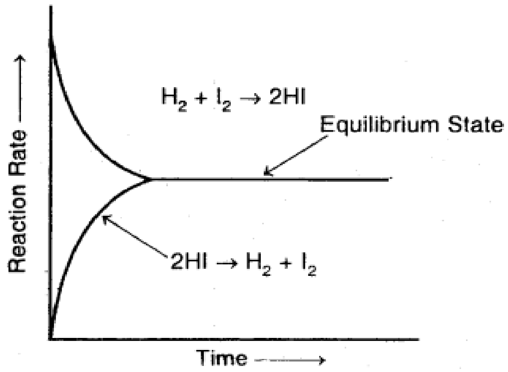
According to Le Chatelier's principle, an increase in the concentration of Cl_2 (one of the products) at equilibrium will favor the backward reaction, and thus the dissociation of PCl_5 into PCl_3 and Cl_2 decreases

Long Answer:

1. **Ans:** Consider the reaction between hydrogen and iodide at a constant temperature of 720 K in a closed vessel. The reaction involved is:

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

Accordingly, the effective collision amongst the reactant molecules will result in the production of HI. Since the product molecules are not permitted to leave the vessel (i.e., the reaction is carried out in a closed vessel), they will also collide amongst themselves leading to the formation of reactant molecules. Under these conditions, the reaction takes place in both directions. Hence, it is called a reversible reaction.



Graphical representation of the change of reaction rates with time for the formation and decomposition of hydrogen iodide

Forward reaction:

$$H_2\,(g) + I_2\,(g) \rightarrow 2HI\,(g)$$

Backward reaction:

$$2HI\,(g) \rightarrow H_2\,(g) + I_2\,(g)$$

Reversible reaction:

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g).$$

To begin with, with the concentration of the reactants being higher in comparison to the product molecules, the rate of the forward reaction will be high as compared to the backward reaction. As the reaction proceeds further, the molar concentration of the reactants will gradually decrease while that of the product will gradually increase.

Apparently, the rate of forwarding reaction goes on decreasing while that of the backward reaction. This state is the reversible chemical reaction is called a chemical equilibrium state.

2. **Ans:** The various factors which influence the equilibrium state are:

   1. **Concentration:** Concentration change influences the equilibrium state. If the concentration of the reactants is increased, the equilibrium will shift in such a direction in which more to the products are formed and vice-versa.

      On the other hand, if the concentration of the products is increased, the equilibrium will shift in such a direction in which more of the reactants are formed.

   2. **Temperature:** Like concentration, the temperature change also affects the equilibrium state. An increase in temperature of the system will shift the equilibrium in such a direction in which heat is absorbed (i.e. rate of endothermic reaction will increase).

      On the other hand, a decrease in temperature of the system will shift the equilibrium in such a direction in which heat is evolved (i.e., rate of exothermic reaction will increase).

   3. **Pressure:** Like concentration and temperature, the pressure also influences

the equilibrium state only when the reaction proceeds with a change in volume. An increase in pressure of the system will shift the equilibrium in such a direction in which the volume of the system decreases.

On the other hand, a decrease in pressure of the system will shift the equilibrium in such a direction in which the volume of the system increases.

To explain the effect of temperature, pressure, and concentration on the equilibrium state, consider the combination of N_2 and H_2 to form NH_3

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g);\ \Delta H = -\,93.6\ kJ$$

The reaction is reversible, exothermic, and accompanied by a decrease in volume.

Effect of temperature: According to Le-Chatelier's principle, an increase in temperature shifts the equilibrium in the direction in which heat is absorbed, and a decrease in temperature shifts the equilibrium in the direction in which heat is evolved. Since the formation of ammonia is accompanied by the evolution of heat, it is favored by a decrease in temperature.

Effect of pressure: According to Le-Chatelier's principle, an increase of pressure on a system in equilibrium, favors the direction which is accompanied by a decrease in volume and vice-versa. While going from, left to right in the above reaction, there is a decrease in the number of moles or say volume, the formation of ammonia is favored by an increase in pressure.

Effect of concentration: According to Le-Chatelier's principle, an increase of concentration of any of the substances in the system shifts the equilibrium in the direction in which the concentration of that substance is reduced. Thus, the addition of N_2 or H_2 favors the formation of ammonia.

3. **Ans:** Salt hydrolysis: Hydrolysis is a process in which a salt reacts with water to form acid and base.

$$\text{Salt + Water} \rightleftharpoons \text{Acid + Base}$$

$$B\,A + H_2O \rightleftharpoons HA + BOH$$

That is the interaction of the cations of the salt with OH ions furnished by water and anions of the salt with H+ ions furnished by water to form an acidic or basic solution is called salt hydrolysis.

(i) Salts of strong acids and strong bases like NaCl, KCl, KNO_3 $NaNO_3$, Na_2SO_4, K_2SO_4 do not undergo hydrolysis because the acids and bases furnished by them in aqueous solutions are strong acids and strong bases which are completely dissociated.

$$NaCl + H_2O \rightleftharpoons NaOH + HCl$$

$$NaOH\ (aq) \rightleftharpoons Na+ + OH-$$

$$HCl\ (Aq) \rightleftharpoons H+ + Cl-$$

Since $[H^+] = [OH-]$ the resulting solution is neutral and its pH = 7.

(iii) Hydrolysis of salts of strong acids and weak bases:

The salts belonging to this type are NH_4NO_3, NH_4Cl, $(NH_4)_2SO_4$, $CuSO_4$, $AlCl_3$, $Ca(NO_3)_2$, etc.

Let us take the case of NH_4NO_3

$$NH_4NO_3 + H_2O \rightleftharpoons NH_4OH + HNO_3$$

$$NH_4+ + NO_3- + H_2O \rightleftharpoons NH_4OH + HNO_3$$

or

$$NH_4+ + H_2O \rightleftharpoons NH_4OH + H+$$

The resulting solution after hydrolysis is basic (pH > 7). Since only the anions of the salt have taken place in the hydrolysis, it is called anionic hydrolysis.

(iv) Hydrolysis of salts of weak acids and weak bases:

The salts belonging to this type are:

CH_3COONH_4, $(NH_4)_2CO_3$, $Ca_3(PO_4)_2$ etc.

Let us take the case of hydrolysis of CH_3COONH_4

$$CH_3COONH_4 + H_3O \rightleftharpoons CH_3COOH + NH_4OH$$

or

$$CH_3CO\bar{O} + NH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

Since both the cations and anions of the salt have participated in the hydrolysis, it is known as cationic as well as anionic hydrolysis. The nature of the solution or pH depends upon the relative strengths of the acid and base that are formed on hydrolysis.

4. **Ans:** Since NaOH is completely ionized

∴ [NaOH] = [OH–] = 10^{-3} N = 10^{-3} M

5. **Ans:** $CH_3COOH \xrightleftharpoons{H_2O} CH_3CO\bar{O} + H_3^+O$

Applying the law of chemical equilibrium

Ka = $[CH_3CO\bar{O}][H_3O^+]/[CH_3COOH]$

$$\therefore \quad [H_3O^+] = \sqrt{K_a[CH_3COOH]}$$

$$\text{as} \quad [CH_3CO\bar{O}] = [H_3O^+]$$

Putting the value of $K_a = 1.8\times10^{-5}$ and

$[CH_3COOH] = 0.01N = 0.01M = 10^{-2}M$

$$[H_3O^+] = \sqrt{1.8\times10^{-5}\times10^{-2}}$$

$$= \sqrt{18}\times10^{-4}\,g \text{ ion L}^{-1}$$

$$p^H = -\log[H_3O^+] = \log(4.242\times10^{-4})$$

$$\therefore \quad = -(0.6276-4) = 3.37$$

Assertion Reason Answer:

1. (i) Both A and R are true and R is the correct explanation of A.
2. (i) Both A and R are true and R is the correct explanation of A.

Case Study Answer:

1. **Answer:**

(1) (a) Low temperature and high pressure

(2) (d) By increasing pressure and decreasing temperature

(3) (b) Low temperature, high pressure and catalyst

(4) (a) Remains constant

(5) (b) $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$

❖❖

Redox Reactions 8

Introduction

Redox reaction is related to gain or loss of electrons. Reaction in which oxidation and reduction takes place simultaneously is called redox reaction. This chapter deals with problems based on redox reactions, oxidation number and balancing of redox reactions by ion, electron method and oxidation number method.

Oxidation Reactions

Oxidation is defined as the addition of oxygen/electronegative element to a substance or removal of hydrogen/ electropositive element from a substance.

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

$$Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$$

Reduction Reactions

Reduction is defined as the removal of oxygen/electronegative element from a substance or addition of hydrogen or electropositive element to a substance.

$$2FeCl_3(aq) + H_2(g) \longrightarrow 2FeCl_2(aq) + 2HCl(aq)$$

$$2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$$

Oxidation Number or Oxidation State

Oxidation number for an element is the arbitrary charge present on one atom when all other atoms bonded to it are removed. For example, if we consider a molecule of HCl, the Cl atom is more electronegative than H-atom, therefore, the bonded electrons will go with more electronegative chlorine atom resulting in formation of H^+ and Cl^- ions. So, oxidation number of H and Cl in HCl are +1 and –1 respectively.

The following points are important to determine the oxidation number of an element.

1. The oxidation number of an atom in pure elemental form is considered to be zero. e.g., H_2, O_2, Na, Mg.
2. Oxidation number of any element in simple monoatomic ion will be equal to the charge on that ion, for example, oxidation number of Na in Na^+ is +1.
3. Oxidation amount of fluorine in its compound with other elements is always -1.
4. Oxidation number of oxygen is generally -2 but in case of peroxide (H_2O_2) oxygen has oxidation number -1. In a compound OF_2 the oxidation number of oxygen is +2.
5. The oxidation number of alkali metals (Na, K) and alkaline earth metals (Ca, Mg) are +1 and +2 respectively.
6. The oxidation number of halogens is generally -1 when they are bonded to less electronegative elements.
7. Oxidation number of hydrogen is generally +1 in most of its compounds but in case of metal hydride (NaH, CaH_2) the oxidation number is hydrogen is -1.
8. The algebraic sum of the oxidation numbers of all the atoms in a neutral compound is zero. In an ion, the algebraic sum of oxidation number is equal to the charge on that ion.

Oxidising and Reducing Agent

A substance which undergoes oxidation acts as a reducing agent while a substance which undergoes reduction acts as an oxidising agent. For example, we take a redox reaction,

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

In this reaction, Zn is oxidised to Zn^{2+} so Zn is reducing agent and Cu^{2+} is reduced to Cu so Cu^{2+} is an oxidising agent.

Types of Redox Reactions

1. **Combination reactions**

   A combination reaction is a reaction in which two or more substances combine to form a single new substance. Combination reactions can also be called synthesis reactions. The general form of a combination reaction is:

   $$A + B \longrightarrow AB$$

   $$Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

2. **Decomposition reactions**

   A decomposition reaction is a reaction in which a compound breaks down into two or more simpler substances. The general form of a decomposition reaction is:

   $$AB \longrightarrow A + B$$

   $$2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$$

3. **Displacement reactions**

   Displacement reaction is a chemical reaction in which a more reactive element displaces a less reactive element from its compound.

   $$CuSO_4(aq) + Zn(s) \longrightarrow ZnSO_4(aq) + Cu$$

4. **Disproportionation reactions**

   The reactions in which a single reactant is oxidized and reduced is known as Disproportionation reactions. The disproportionation reaction is given below.

   $$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Balancing of Redox Reactions

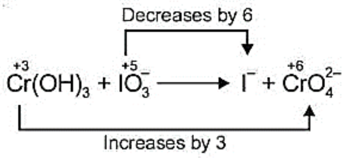
a. Oxidation Number Method

In this method number of electrons lost in oxidation must be equal to number of electrons gained in reduction. Following rules are followed for balancing of reactions:

1. Write the skeletal equation of all the reactants and products of the reaction.
2. Indicate the oxidation number of each element and identify the elements undergoing change in oxidation number.
3. Equalize the increase or decrease in oxidation number by multiplying both reactants and products undergoing change in oxidation number by a suitable integer.
4. Balance all atoms other than H and O, then balance O atom by adding water molecules to the side short of O-atoms.
5. In case of ionic reactions:
   - **i. For acidic medium:** First balance O atoms by adding H_2O molecules to the side deficient in O atoms and then balance H-atoms by adding H+ ions to the side deficient in H atoms.
   - **ii. For basic medium:** First balance O atoms by adding H_2O molecules to whatever side deficient in O atoms. The H atoms are then balanced by adding H_2O molecules equal in number to the deficiency of H atoms and an equal number of OH– ions are added to the opposite side of the equations.

Balance the ionic equation in alkaline medium

$$Cr(OH)_3 + IO_3^- \longrightarrow I^- + CrO_4^{2-}$$



$$2Cr(OH)_3 + IO_3^- \longrightarrow I^- + 2CrO_4^{2-}$$

Balancing of O and H

$$2Cr(OH)_3 + IO_3^- + 4OH^- \longrightarrow I^- + 2CrO_4^{2-} + H_2O + 4H_2O$$

Now, $2Cr(OH)_3 + IO_3^- + 4OH^- \longrightarrow I^- + 2CrO_4^{2-} + 5H_2O$

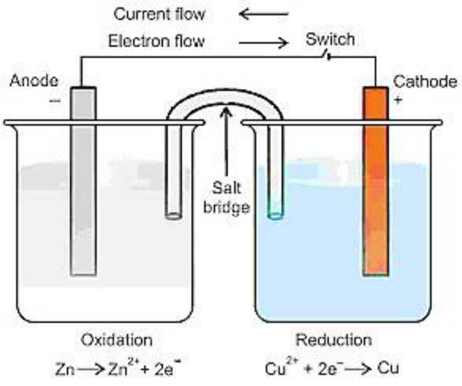
b. Ion-Electron Method

1. Write the skeleton equation and indicate the oxidation number of all the elements which appear in the skeletal equation above their respective symbols.
2. Find out the species which are oxidised and which are reduced.
3. Split the skeleton equation into two half reactions, i.e., oxidation half reaction and reduction half reaction.
4. Balance the two half reaction equations separately by the rules described below:
   i. In each half reaction, 1st balance the atoms of the elements which have undergone a change in oxidation number.
   ii. Add electrons to whatever side is necessary to make up the difference in oxidation number in each half reaction.
   iii. Balance oxygen atoms by adding required number of H_2O molecules to the side deficient in O atoms.
   iv. In the acidic medium, H atoms are balanced by adding H^+ ions to the side deficient in H-atoms. However, in the basic medium, H atoms are balanced by adding H_2O molecules equal in number to the deficiency of H atoms and an equal number OH^- ions are included in the opposite side of the equation.
5. The two half reactions are then multiplied by suitable integers so that the total number of electrons gained in one half of the reaction is equal to the number of electrons lost in the other half reaction. The two half reactions are then added up.
6. To verify whether the equation thus obtained is balanced or not, the total charge on either side of the equation must be equal.

Galvanic Cell and Electrode Potential

A galvanic cell or voltaic cell is simple electrochemical cell in which a redox reaction is used to convert chemical energy into electrical energy. It means electricity can be generated with the help of redox reaction in which oxidation and reduction takes place in two separate compartments. Each compartment consists of a metallic conductor and dipped in suitable electrolytic solution of same metal. Metallic rod acts as electrode.

The compartment having electrode dipped in solution of electrolyte is known as half-cell and a half cell has a redox couple. A redox couple means a solution having reduced and oxidised form of a substance together, taking part in oxidation or reduction half reaction. It is depicted as M^{+n} / M i.e., oxidised form / reduced form. To prepare a galvanic cell two half cells are externally connected through a conducting wire and internally through salt bridge.



Anodic oxidation: $Zn_2 \longrightarrow Zn^{+2}(aq) + 2e(s)$

Cathodic reduction: $Cu^{+2}(aq) + 2e \longrightarrow Cu(s)$

Net reaction: $Zn(s) + Cu^{+2}(aq) \longrightarrow Zn^{+2}(aq) + Cu(s)$

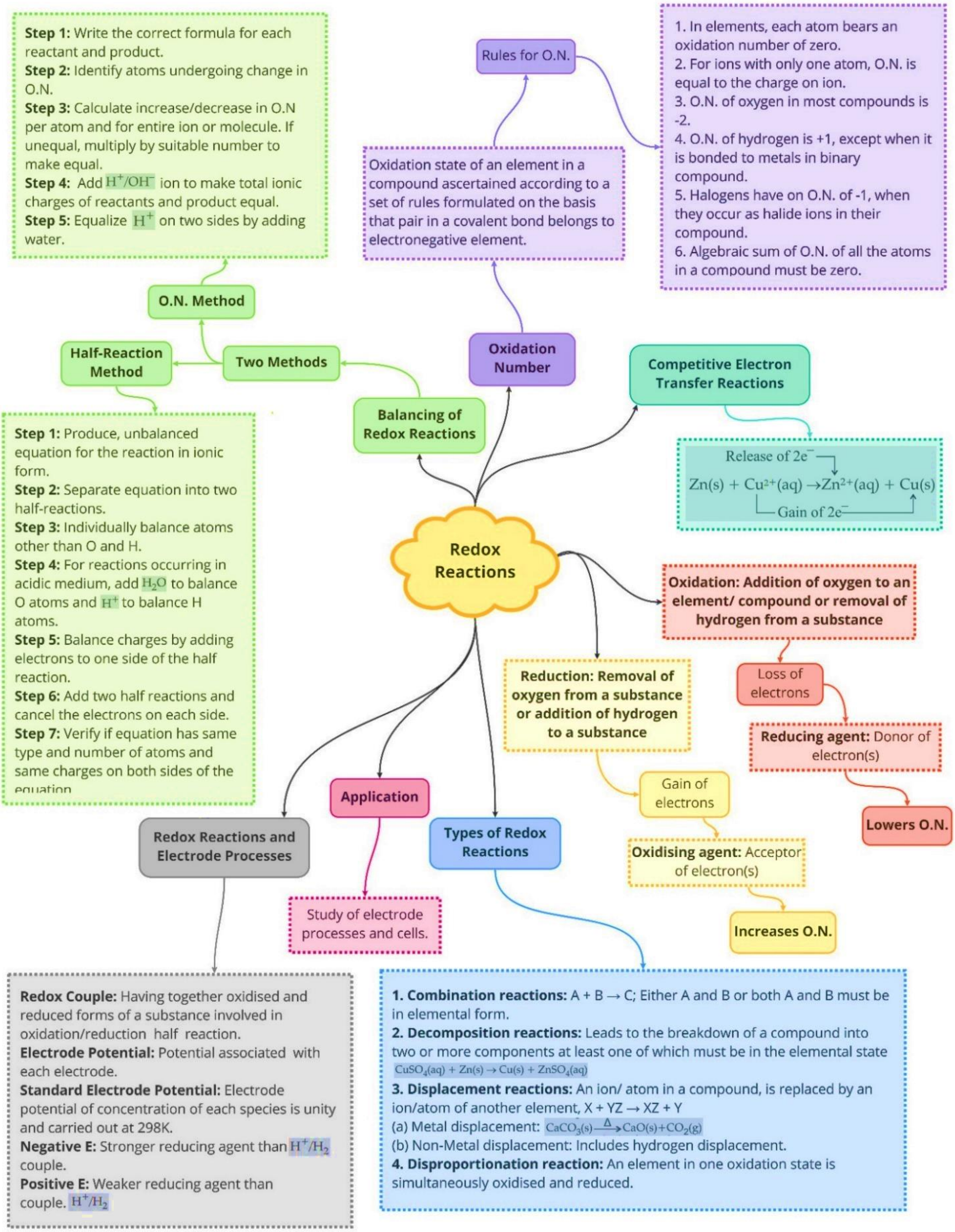
This cell can be briefly presented in one line, known as cell notation *i.e.,*

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

Summary-

1. **Oxidation number:** Charge on atom which appears on it when it is present in the combined state.
2. Sum of the oxidation states in a compound/ion should be equal to the zero or to the net charge on the ion.
3. Some elements show variable oxidation states.
4. **Oxidation:** The process in which electrons are lost.
5. **Reduction:** The process in which electrons are gained.
6. **Oxidising agent:** A substance which oxidises the other.
7. **Reducing agent:** A substance which reduces the other.
8. **Redox reaction:** When oxidation and reduction take place together is known as redox reaction.
9. **Disproportionation reaction:** The reaction in which same species is simultaneously oxidised as well as reduced.
10. The change in oxidation state of any element in a compound is useful in calculating the equivalent weight.
11. **Electrochemical series:** Arrangement of E°red of different electrodes in increasing order of electrode potential.
12. **Electrode Potential:** The tendency of an electrode to lose or gain electrons is called electrode potential.
13. The standard electrode potentials of a large number of electrodes have been determined using standard hydrogen electrode as the reference electrode. By convention, the standard electrode potential (E°) of hydrogen electrode is 0.00 volts.

Class : 11th Chemistry
Chapter- 8: Redox Reactions



Redox Reactions

Oxidation Number

Oxidation state of an element in a compound ascertained according to a set of rules formulated on the basis that pair in a covalent bond belongs to electronegative element.

Rules for O.N.

1. In elements, each atom bears an oxidation number of zero.
2. For ions with only one atom, O.N. is equal to the charge on ion.
3. O.N. of oxygen in most compounds is -2.
4. O.N. of hydrogen is +1, except when it is bonded to metals in binary compound.
5. Halogens have on O.N. of -1, when they occur as halide ions in their compound.
6. Algebraic sum of O.N. of all the atoms in a compound must be zero.

Balancing of Redox Reactions

Two Methods

O.N. Method

Step 1: Write the correct formula for each reactant and product.
Step 2: Identify atoms undergoing change in O.N.
Step 3: Calculate increase/decrease in O.N per atom and for entire ion or molecule. If unequal, multiply by suitable number to make equal.
Step 4: Add H^+/OH^- ion to make total ionic charges of reactants and product equal.
Step 5: Equalize H^+ on two sides by adding water.

Half-Reaction Method

Step 1: Produce, unbalanced equation for the reaction in ionic form.
Step 2: Separate equation into two half-reactions.
Step 3: Individually balance atoms other than O and H.
Step 4: For reactions occurring in acidic medium, add H_2O to balance O atoms and H^+ to balance H atoms.
Step 5: Balance charges by adding electrons to one side of the half reaction.
Step 6: Add two half reactions and cancel the electrons on each side.
Step 7: Verify if equation has same type and number of atoms and same charges on both sides of the equation

Competitive Electron Transfer Reactions

$$\underbrace{\overbrace{Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq)}^{\text{Release of } 2e^-} + Cu(s)}_{\text{Gain of } 2e^-}$$

Oxidation: Addition of oxygen to an element/ compound or removal of hydrogen from a substance

Loss of electrons

Reducing agent: Donor of electron(s)

Lowers O.N.

Reduction: Removal of oxygen from a substance or addition of hydrogen to a substance

Gain of electrons

Oxidising agent: Acceptor of electron(s)

Increases O.N.

Types of Redox Reactions

1. Combination reactions: A + B → C; Either A and B or both A and B must be in elemental form.
2. Decomposition reactions: Leads to the breakdown of a compound into two or more components at least one of which must be in the elemental state $CuSO_4(aq) + Zn(s) \rightarrow Cu(s) + ZnSO_4(aq)$
3. Displacement reactions: An ion/ atom in a compound, is replaced by an ion/atom of another element, X + YZ → XZ + Y
(a) Metal displacement: $CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$
(b) Non-Metal displacement: Includes hydrogen displacement.
4. Disproportionation reaction: An element in one oxidation state is simultaneously oxidised and reduced.

Application

Study of electrode processes and cells.

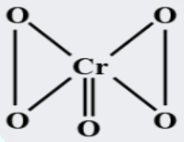
Redox Reactions and Electrode Processes

Redox Couple: Having together oxidised and reduced forms of a substance involved in oxidation/reduction half reaction.
Electrode Potential: Potential associated with each electrode.
Standard Electrode Potential: Electrode potential of concentration of each species is unity and carried out at 298K.
Negative E: Stronger reducing agent than H^+/H_2 couple.
Positive E: Weaker reducing agent than couple. H^+/H_2

Important Questions

Multiple Choice questions-

1. $KMnO_4$ reacts with oxalic acid according to the equation $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$ Here 20 mL of 0.1 M $KMnO_4$ is equivalent to
   (a) 50 mL of 0.5 M $C_2H_2O_4$
   (b) 20 mL of 0.1 M $C_2H_2O_4$
   (c) 20 mL of 0.5 M $C_2H_2O_4$
   (d) 50 mL of 0.1 M $C_2H_2O_4$
2. Which of the following is a redox reaction?
   (a) $NaCl + KNO_3 \rightarrow NaNO_3 + KCl$
   (b) $Mg(OH)_2 + 2NH_4Cl \rightarrow MgCl_2 + 2NH_4OH$
   (c) $CaC_2O_4 + 2HCl \rightarrow CaCl_2 + H_2C_2O_4$
   (d) $2Zn + 2AgCN \rightarrow 2Ag + Zn(CN)_2$
3. The reduction potential values of M, N and O are +2.46 V, -1.13 V, -3.13 V respectively. Which of the following orders is correct regarding their reducing property?
   (a) O > N > M
   (b) M > O > N
   (c) M > N > O
   (d) O > M > N
4. Which of the following processes does not involve either oxidation or reduction?
   (a) Formation of slaked lime from quick lime
   (b) Heating Mercuric Oxide
   (c) Formation of Manganese Chloride from Manganese oxide
   (d) Formation of Zinc from Zinc blende
5. The number of moles of $KMnO_4$ reduced by one mole of KI in alkaline medium is
   (a) One
   (b) Two
   (c) Five
   (d) One fifth.
6. What is known as Autooxidation?
   (a) Formation of H_2O by the oxidation of H_2O_2.
   (b) Formation of H_2O_2 by the oxidation of H_2O.
   (c) Both (1) and (2) are true
   (d) None of the above
7. Which of the following statements regarding sulphur is incorrect?
   (a) S_2 molecule is paramagnetic.
   (b) The vapour at 200° C consists mostly of S_8 rings.
   (c) At 600°C the gas mainly consists of S_2 molecules.
   (d) The oxidation state of Sulphur is never less than +4 in its compounds.
8. The oxidation number of Xe in $BaXeO_6$ is
   (a) 8
   (b) 6
   (c) 4
   (d) 10
9. CrO_5 has structure as shown, the oxidation number of chromium in the compound is?



   (a) +10
   (b) +6
   (c) +4
   (d) +5
10. Pure water is bad conductor of electricity because
   (a) It has high boiling point
   (b) It is almost unionised
   (c) Its molecules are associated with H- bonds
   (d) Its pH is 7 at 25°C
11. The oxidation process involves
   (a) Increase in oxidation number
   (b) Decrease in oxidation number
   (c) No change in oxidation number
   (d) None of the above
12. The ionic mobility of alkali metal ions in aqueous solution is maximum for
   (a) Li^+
   (b) Na^+
   (c) K^+
   (d) Rb^+

13. Pure water is bad conductor of electricity because
    (a) It has high boiling point
    (b) It is almost unionised
    (c) Its molecules are associated with H- bonds
    (d) Its pH is 7 at 25°C
14. The oxidation number of Fe in $K_4\,[Fe\,(CN)_6]$ is
    (a) 3
    (b) 4
    (c) 2
    (d) Zero
15. A standard hydrogen electrode has zero electrode potential because
    (a) Hydrogen is easiest to oxidise
    (b) This electrode potential is assumed to be zero
    (c) Hydrogen atom has only one electron
    (d) Hydrogen is the lightest element

Very Short:

1. What are redox reactions? Give an example.
2. Define oxidation and reduction in terms of electrons.
3. Define an oxidizing agent. Name the best oxidizing agent.
4. What is meant by reducing agent? Name the best reducing agent.
5. In the reaction $MnO_2 + 4HCl \rightarrow MnCl_2 + H_2O$ which species is oxidized?
6. What is the oxidation state of Ni in $Ni\,(CO)_4$?
7. What is a redox couple?
8. Define oxidation and reduction in the term of oxidation numbers.
9. What is the sum of oxidation numbers of all atoms in $HIO_4$4?
10. What is the oxidation number of N in $(NH_4)_2\ SO_2$?

Short Questions:

1. HNO_3 acts only as an oxidant whereas HNOz acts both as an oxidant and reductant. Why?
2. Balance the following equation by the ion-electron method.

   $Zn(s) + NO^{3-} \rightarrow Zn^{2+}(aq) + NH+\,(aq) + H_2O(l)$ (In acid solution)
3. Balance the following equation in acidic medium by oxidation number method.
4. Indicate the oxidising and reducing agent in the following reactions:
5. Which of the following redox reaction is oxidation & which is reduction?
6. What are the minimum and maximum oxidation numbers shown by sulfur?

Long Questions:

1. What are the minimum and maximum oxidation numbers shown by sulfur?
2. Starting with the correctly balanced half-reaction, write the overall net ionic equation for the following change:
3. Write the method used for balancing redox reaction by oxidation number method.
4. Determine the oxidation number of O in the following: OF_2, Na_2O_2 & CH_3COOH

   (i) OF_2

   (ii) Na_2O_2

   (ii) CH_3COOH
5. Determine the volume 6f M/8 $KMnO_4$ solution required to react completely with 25.0 cm3 of M/4 $FeSO_4$ solution in an acidic medium.

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): Among halogens fluorine is the best oxidant.

   Reason (R): Fluorine is the most electronegative atom.

   (i) Both A and R are true and R is the correct explanation of A.
   (ii) Both A and R are true but R is not the correct explanation of A.
   (iii) A is true but R is false.
   (iv) Both A and R are false.
2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): In the reaction between potassium permanganate and potassium iodide, permanganate ions act as oxidising agent.

   Reason (R): Oxidation state of manganese changes from +2 to +7 during the reaction.

(i) Both A and R are true and R is the correct explanation of A.

(ii) Both A and R are true but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) Both A and R are false.

Case Study Based Question:

1. Read the passage given below and answer the following questions:

The oxidation state of an individual atom is 0. The total oxidation state of all atoms in a neutral species is 0 and in an ion is equal to the ion charge. Group 1 metals have an oxidation state of + 1 and group 2 an oxidation state of + 2.

The oxidation state of fluorine is – 1 in compounds. Hydrogen generally has an oxidation state of + 1in compounds. Oxygen generally has an oxidation state of – 2 in compounds.

In binary metal compounds, group 17 elements have an oxidation state of – 1, group 16 elements of – 2, and group 15 elements of – 3. The sum of the oxidation states is equal to zero for neutral compounds and equal to the charge for polyatomic ion species. An atom is oxidised if its oxidation number increases and an atom is reduced if its oxidation number decreases.

The atom that is oxidised is the reducing agent and the atom that is reduced is the oxidising agent.

(1) One mole of acidified $K_2 Cr_2 O_7$ on reaction with excess KI will liberate n mole of I_2 then the value of n is:

(a) 6

(b) 1

(c) 3

(d) 7

(2) When electrons are transferred from Zn to Cu^{2+} in copper sulphate solution, the energy (heat) is:

(a) Absorbed

(b) Evolved

(c) Consumed

(d) Both (a) and (b)

(3) Negative $E^{\ominus}$ indicates that redox couple is

(a) Weaker reducing agent than H^+/ H_2 couple

(b) Stronger reducing agent than H^+/ H_2 couple

(c) Stronger oxidising agent than H^+/ H_2 couple

(d) Weaker oxidising agent than H^+/ H_2 couple

(4) Which of the following statements is/are incorrect?

(a) The reactants, which undergo oxidation and reduction are called reductant and oxidant respectively

(b) In redox reaction, the oxidation number of oxidant increases, while that of reductant decreases

(c) HNO_2 acts as an oxidising as well as reducing agent

(d) Oxidation is the process, in which electrons are lost

2. Read the passage given below and answer the following questions:

The concept of electron transfer is found unable to explain the redox changes or electron shift in case of covalent compounds.

To explain these changes a new concept, called oxidation number is introduced. Oxidation number is defined as the charge that an atom of the element has in its ion or appear to have when present in the combined state with other atoms. In other words, it is also defined as the charge that an atom appears to have in a compound when all other atoms are removed as ions from the compound.

The following steps are involved while calculating the oxidation number of an atom in a given compound/ ion.

Step-I Write down the formula of given compound/ion leaving some space between the atoms.

Step-II Write the oxidation state of each element above its atoms. Write down x above the atom, oxidation state of which we have to find out.

Step-III Multiply the oxidation numbers of each element with the number of atoms of that element present in the compound. Enclose the product in a bracket.

Step-IV Equate the algebraic sum of the oxidation numbers of all the atoms present in compound to zero or to the charge in case of ionic species charge on the ion.

Step-V Solve the equation obtained for the value of x.

(1) Highest oxidation state of Mn is present in:

(a)$KMnO_4$

(b)K_2MnO_4

(c)M_2nO_3

(d)MnO_2

(2) Identify the element which never has positive oxidation number in any of its compound?

(a) Oxygen

(b) Chlorine

(c) Fluorine

(d) Bromine

(3) When a manganous salt is fused with a mixture of KNO_3 and solid NaOH, the oxidation number of Mn changes, from + 2 to:

(a) + 4

(b) + 3

(c) + 6

(d) + 7

(4) The brown ring complex compound is formulated as $[Fe(H_2O)_5\ NO]SO_4$. What will be the oxidation state of iron in the given complex?

(a) + 2

(b) + 3

(c) + 4

(d) + 1

Answer Key

MCQ

1. (d) 50 mL of 0.1 $MC_2H_2O_4$
2. (d) $2Zn + 2AgCN \rightarrow 2Ag + Zn(CN)_2$
3. (d) O > M > N
4. (a) Formation of slaked lime from quick lime
5. (b) Two
6. (b) Formation of H_2O_2 by the oxidation of H_2O.
7. (d) The oxidation state of sulphur is never less than +4 in its compounds.
8. (d) 10
9. (b) +6
10. (b) It is almost unionised
11. (a) Increase in oxidation number
12. (d) Rb^+
13. (b) It is almost unionised
14. (c) 2
15. (b) This electrode potential is assumed to be zero

Very Short Answer:

1. Redox reaction is a reaction in which oxidation and reduction take place simultaneously, e.g.

   $Zn\ (s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
2. Oxidation involves loss and reduction involves the gain of electrons.
3. The oxidizing agent is a substance that can gain electrons easily. F_2 is the best oxidizing agent.
4. The reducing agent is a substance that can lose electrons easily. Li is the best reducing agent

   (ii) Dissociation increases, i.e., the equilibrium shifts forward.
5. HCl is oxidized to Cl_2
6. Zero
7. The redox couple consists of the oxidized and reduced form of the same substance taking part in an oxidation or reduction half-reaction, for example.

   $Zn^{2+}(aq)\ /\ Zn,\ Cl_2\ /\ Cl^-(aq)$ etc.

8. Oxidation involves an increase in oxidation number while reduction involves a decrease in oxidation number.

$$Sn^{2+} + 2Hg^{2+} \rightarrow Sn^{4+} + Hg^{2+}$$

Here Sn^{2+} gets oxidised while Hg^{2+} gets reduced.

9. Zero

10.

$$\overset{x+1}{(NH_4)_2}\overset{-2}{SO_4}$$

$$2x+8(+1)-2=0$$

$$2x+8-2=0$$

$$x=-3$$

The oxidation number of N is $(NH_4)_2 SO_4$ is – 3.

Short Answer:

1. **Ans:** Ox. No. of N in HNO_3 = +5

Ox No. of N in HNO_2 = +3

Maximum oxidation numbers which N can show is = + 5

(∴ It has only 5 valance electrons $2S^2 2P^3$)

The Ox. No. of N in HNO_3 is maximum and it can only decrease. Therefore, HNO_3 can act only as an oxidant. Minimum Ox. No. of N is -3.

Thus, HNO_2 in which Ox. No. of N is +3 Can decrease as well as increase. Thus, HNO_2 can act as an oxidant as well as a reductant.

2. **Ans:** Oxidation half reaction

$$Zn(s) \longrightarrow Zn^{2+}(aq)$$

$$Zn(s) \longrightarrow Zn^{2+} + 2e^-$$

(To balance charge) ...(1)

Reduction half reaction

$$NO_3^-(aq) \longrightarrow NH_4^+(aq)$$

$$NO_3^-(aq) \longrightarrow NH_4^+ + 3H_2O(l)$$

(to balance O atom)

$$NO_3^-(aq) + 10H^+(aq) \longrightarrow NH_4^+(aq) + 3H_2O(l)$$

(to balance H atom)

$$NO_3^-(aq) + 10H^+(aq) + 8e^- \longrightarrow NH_4^+ + 3H_2O(l)$$

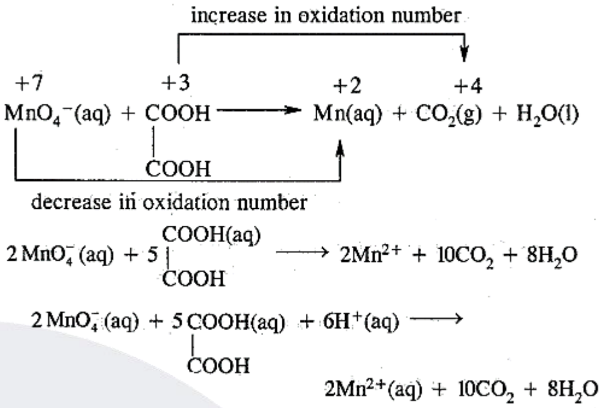
Multiply (1) equation by 4 to equalize the no. of electron in both. Add both half reaction

$$4\,Zn(s) \rightarrow Zn^{2+}(aq) + 8e-$$

$$Zn(s) + NO_3-\ (aq) + 10H+\ (aq) \rightarrow 4Zn^{2+}\ (aq) + NH^+(aq) + 3H_2O(1)$$

– 1 + 10 = + 8 + 1+ 9 = + 9

3. **Ans:**



4. **Ans:**

(i) $2Mg + SO_2 \rightarrow 2MgO + S$

Mg = Reducing agent

SO_2 = Oxidising agent

(ii) $2Cu^{2+} + 41 \rightarrow 2CuI + I_2$

Cu^{2+} = Oxidising agent

I- = Reducing agent

(iii) $SO_2 + 2H_2S \rightarrow 2H_2O + 3S$

SO_2 = Oxidising agent

H_2S = Reducing agent

(iv) $Sn^{2+} + 2Hg^{2+} \rightarrow Hg2^{2+} + Sn^{4+}$

Sn^{2+} = Reducing agent

Hg^{2+} = Oxidising agent

5. **Ans:**

(i) $Zn \rightarrow Zn^{2+} + 2e^-$

Oxidation

(ii) $Cl_2 + 2e^- \rightarrow 2Cl-$

Reduction

(iii) $Fe \rightarrow Fe^{2+} + 2e^-$

Oxidation

(iv) $Sn^{4+} + 2e^- \rightarrow Sn^{2+}$

Reduction

6. **Ans:** The minimum oxidation number shown by S is – 2 since it can acquire 2 more electrons to achieve the nearest inert gas [Ar] configuration.

The maximum Ox. No. shown by S is +6 since it has 6 valance electrons. ($3S^2\ 3P^4$)

Long Answer:

1. **Ans:** Various atoms are assigned oxidation number on the basis of the following rules:

1. An element in the free state has an oxidation number equal to zero, e.g., H_2, He, K, Ag all have zero ox. no.
2. In a binary compound of a metal and a non-metal, the oxidation number of metal is positive while that of non-metal is negative. In NaCl the ox. no. of sodium +1 and ox. n. of chlorine is –1.
3. In a covalent compound, the atom with higher electronegativity has a negative oxidation number while another atom has a positive oxidation number.
4. The oxidation number of the radical or ions is equal to the electrical charge on it. for e.g., the ox. no. of Na+ is +1.
5. In neutral molecules, the algebraic sum of the oxidation number of all the atoms is zero.

2. **Ans:** The skeletal equation is

$MnO_4^- + H^+ + Cl^-(aq) \rightarrow Mn^{2+} + Cl_2(g) + H_2O\ (l)$

Ox. no. of Mn change from +7 in MnO_4^- to +2

Whereas ox. no. of chlorine changes from -1 in Cl^- ions to 0 in Cl_2.

$$Mn \downarrow 5\times 2$$

$$2Cl \longrightarrow Cl_2 \uparrow 2\times 5$$

$$2MnO_4^-(aq)+10Cl^-(aq)\longrightarrow 2Mn^{2+}(aq)+5Cl_2(g)$$

(To balance O atoms)

$$2MnO_4^-(aq)+10Cl^-(aq)\longrightarrow 2Mn^{2+}(aq)+5Cl_2+8H_2O$$

$$2MnO_4^-(aq)+10Cl^-(aq)+16H^+\longrightarrow 2Mn^{2+}+5Cl_2+H_2O$$

(to balance H atoms)

3. **Ans:** The following steps are used for balancing the reactions by these methods:

1. Writing the skeletal equation for all the reactants and products of the reaction.
2. Assignment of the oxidation number of all atoms in each compound in the skeletal equation. Identify the atoms undergoing a change in their oxidation number.
3. Calculating the increase or decrease in oxidation number per atom and then for the whole molecule in which it occurs. If these are not equal, then multiplying by suitable coefficients such that these become equal.
4. Now balancing the chemical reaction with respect to all atoms except H & O.
5. Finally balancing with respect to H & O atom for balancing oxygen atoms add H20 molecules to the side deficient in it.

4. **Ans:**

(i) OF_2

Let the ox. no. of O = x

The ox. no. of each F = –1

x – 2 = 0

x = +2

(ii) Na_2O_2

Let the o. no. of O = x

ox. no. of each Na = + 1

2 + 2x = 0

2x = – 2

x = – 1

(iii) CH_3COOH

Let the ox. no. of O = x

The ox. no. of each carbon atom = –1

The ox. no. of hydrogen = +1

– 2 + 4 + 2x = 0

2x + 2 = 0

x = – 1

5. **Ans:** The balanced ionic equation for the reaction is

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

from the balanced equation, it is evident that-

1 mole of $KMnO_4$ = 5 moles of $FeSO_4$

Applying the molarity equation to the balanced redox equation.

$$\frac{M_1V_1}{n_1}(KMnO_4)=\frac{M_2V_2}{n_2}(FeSO_4)$$

or $$\frac{1\times V_1}{8\times 1}=\frac{1}{4}\times\frac{25}{5}$$

or $$V_1=\frac{1\times 25\times 8}{4\times 5}$$

$= 10.0\ cm^3$

Thus, the volume of M/8 $KMnO_4$ solution required = 10.0 ml.

Assertion Reason Answer:

1. (ii) Both A and R are true but R is not the correct explanation of A.
2. (iii) A is true but R is false.

Case Study Answer:

1. **Answer:**
   (1) (c) 3
   (2) (b) Evolved
   (3) (b) Stronger reducing agent than H^+/H_2 couple
   (4) (b) In redox reaction, the oxidation number of oxidant increases, while that of reductant decreases

2. **Answer:**
   (1) (a)$KMnO_4$
   (2) (c) Fluorine
   (3) (c) + 6
   (4) (b) + 3

❖ ❖

Hydrogen

9

Introduction

In this chapter we will study the preparation, properties of dihydrogen and of some important compounds formed by hydrogen like H_2O and H_2O_2.

Hydrogen is the first element of the periodic table. The atomic structure of hydrogen is the simplest one with only one proton and one electron. Hydrogen occurs in its atomic form only at very high temperatures. Water is one of the most important compounds formed by hydrogen. Even its name hydrogen was given by Lavoisier because of its ability to form water as in Greek, hydro means water and gene means forming.

Position of Hydrogen in the Periodic Table

Hydrogen is the first element in the periodic table. The electronic configuration of hydrogen is $1s^1$, yet its position in the periodic table is not certain and unsatisfactory. Hydrogen exhibits properties similar to both alkali metals (Group 1) and halogens (Group 17).

Resemblance with Alkali Metals

Like alkali metals, hydrogen has only one electron in its outer shell.

Alkali metals have a strong tendency to lose one electron from their outermost shell. Similarly, hydrogen also loses electron to form H^+ ion.

Alkali metals form stable oxides, halides and sulphides. Similarly, hydrogen also forms stable oxide (H_2O), halides (HF) and sulphide (H_2S).

Resemblance with Halogens

Halogens have a tendency to gain one electron. Similarly, hydrogen ($1s^1$) gains one electron to form H^- ion.

Hydrogen molecule is diatomic (H_2) and so are the molecules of halogens (say F_2).

Hydrogen forms hydrides with carbon (e.g., CH_4), just like halogens form halides with carbon (CCl_4).

Isotopes of Hydrogen

Isotopes are the different forms of the same element having same atomic number but different mass numbers. There are three isotopes of hydrogen namely protium, deuterium and tritium.

1. **Protium or ordinary hydrogen ($_1H^1$):** It has one proton and no neutron in the nucleus and one electron revolves around the nucleus.
2. **Deuterium ($_1H^2$ or D):** It is also known as heavy hydrogen. It has one proton and one neutron in the nucleus around which one electron revolves.
3. **Tritium ($_1H^3$ or T):** This isotope of hydrogen is radioactive and emits low energy $\beta-$ particles having half-life period of 12.33 years. It has one proton and two neutrons in the nucleus. The concentration of tritium is very low.

Dihydrogen

Occurrence

Dihydrogen is the most abundant element in the universe. It constitutes about 70% of the total mass of the universe. But its abundance in earth's atmosphere is very less. It is just 0.15% by mass in the earth's atmosphere.

In free state hydrogen is present in volcanic gases and in the combined form it constitutes 15.4% of the earth's crust and the oceans. However, it is also present in the plant and animal tissues, carbohydrates, proteins etc. Even hydrogen is present in mineral resources like coal and petroleum.

Hydrogen is the principal element in the solar atmosphere. It is present in the outer atmosphere of Sun and other stars of the universe+ like Jupiter and Saturn.

Preparation of Dihydrogen

1. **Laboratory Preparation of Dihydrogen**
   - i. In laboratory dihydrogen is prepared by the reaction of granulated zinc with dilute hydrochloric acid or dilute sulphuric acid.

$$Zn + 2H^{+}(dil) \longrightarrow Zn^{2+} + H_2$$

   - ii. Zinc reacts with aqueous alkali to give dihydrogen

$$Zn + 2NaOH \longrightarrow Na_2ZnO + H_2$$

2. **Commercial Production of Dihydrogen**
   - i. **By the electrolysis of water:** Electrolysis of acidified water using platinum electrodes is used for the bulk preparation of hydrogen.

$$2H_2O \longrightarrow 2H_2 + O_2$$

   - ii. **By the action of steam on coke:** Dihydrogen is prepared by passing steam over coke or hydrocarbons at high temperature (1270 K) in the presence of Nickel catalyst.

$$C + H_2O \longrightarrow CO + H_2$$

The mixture of CO(g) and H_2(g) is called water gas. It is also known as synthesis gas or simply 'syn gas' because it is used in the synthesis of methanol and many other hydrocarbons.

Properties of Dihydrogen

i. **Physical Properties**

- Dihydrogen is a colorless, odourless, tasteless, combustible gas.
- It is lighter than air.
- It is insoluble in water.

ii. **Chemical Properties**

Reaction with halogens: It reacts with halogens, X_2 to give hydrogen halides, HX,

$$H_2 + X_2 \longrightarrow 2HX \text{ (X F,Cl, Br,I)}$$

Reaction with dioxygen: It reacts with dioxygen to form water. The reaction is highly exothermic.

$$2H_2 + O_2 \longrightarrow 2H_2O$$

Reaction with dinitrogen: With dinitrogen it forms ammonia.

$$3H_2 + N_2 \longrightarrow NH_3$$

Reactions with metals: Dihydrogen reacts with metals to yield hydrides at high temperature.

$$H_2 + 2M(g) \longrightarrow 2MH(s)$$

where M is an alkali metal.

Hydrogenation of vegetable oils: Edible oils (unsaturated) like cotton seed oil, groundnut oil are converted into solid fat (saturated) also called vegetable ghee by passing hydrogen through it in the presence of Ni at 473 K.

$$\text{Vegetable oil} + H_2 \longrightarrow \text{Fat}$$

Uses of Dihydrogen

1. **Synthesis of ammonia:** Dihydrogen is used in Haber's process in the synthesis of ammonia.
2. **Hydrogenation of oils:** Dihydrogen is added to oils like soyabean oil, cotton seed oil for manufacturing vanaspati fat.
3. **Manufacture of methyl alcohol:** Water gas enriched with hydrogen gas in the presence of cobalt catalyst gives methanol.
4. **Manufacture of hydrogen chloride:** It is used in the manufacturing of hydrogen chloride which is a very important chemical.
5. **Manufacture of metal hydrides:** It is used in the manufacture of many metal hydrides.
6. **Metallurgical processes:** Since, dihydrogen is used to reduce heavy metal oxides to metals, as it is a reducing agent. Therefore, it finds its use in metallurgical processes.
7. **Rocket fuel:** It is used as a rocket fuel for space research in the form of liquid hydrogen and liquid oxygen.
8. **Fuel Cells:** Dihydrogen is used in fuel cells for the generation of electrical energy.
9. It is used in the atomic hydrogen torch and oxyhydrogen torches for cutting and welding purposes.

Hydrides

Hydrogen combines with a large number of other elements including metals and non-metals, except noble gases to form binary compounds called hydrides. If 'E' is the symbol of the element then hydrides are represented as EH_x (e.g., BeH_2)

Based on their physical and chemical properties, the hydrides have been classified into three main categories:

- Ionic or saline or salt like hydrides.
- Covalent or molecular hydrides.
- Metallic or non-stoichiometric hydrides.

Ionic or Saline Hydrides

The ionic hydrides are stoichiometric which are formed when hydrogen combines with elements of s-block elements except Be. Ionic hydrides are formed by transfer of electrons from metals to hydrogen atoms and contain hydrogen as H– ion e.g., sodium hydride (Na^+H^-)

Covalent or Molecular Hydrides

Covalent or molecular hydrides are the compounds of hydrogen with p-block elements. The most common hydrides are CH_4, H_2O, NH_3 etc. Covalent hydrides are volatile compounds.

Metallic or Non-Stoichiometric Hydrides

The elements of group 3, 4, 5 (d-block) and f-block elements form metallic hydrides. In group 6, only chromium forms hydride (CrH). Metals of group 7, 8, 9 do not form hydrides. These hydrides are known as metallic hydrides because they conduct electricity.

Water

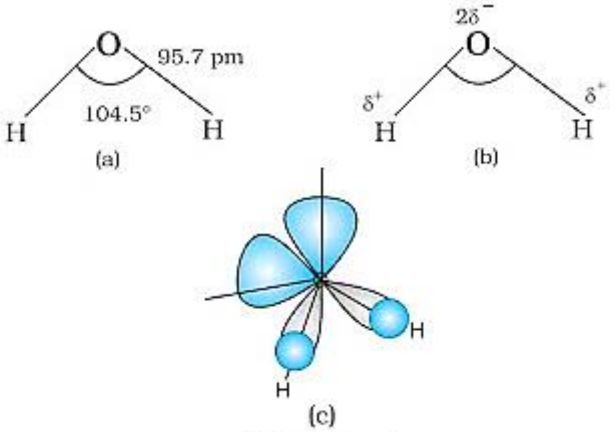
Water is an oxide of hydrogen. It is an important component of all living organisms. Water constitutes about 65% of human body and 95% of plants. It is therefore essential for life. The ability of water to dissolve so many other substances makes it a compound of great importance. Almost three-fourth of the earth's surface is covered with water.

Physical Properties of Water

1. Pure water is colourless, odourless and tasteless.
2. Water is present in the liquid state at room temperature.

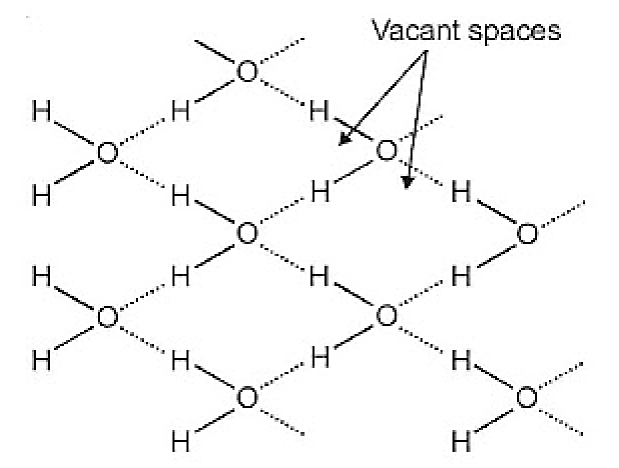
3. Water boils at 100°C and changes into the gaseous state whereas it freezes at 0°C to form ice.
4. Water molecules undergo extensive hydrogen bonding.
5. It is an excellent solvent for many thing like alcohols and carbohydrates dissolve in water.

Structure of Water



H_2O molecule

Structure of Ice



Chemical Properties

1. **Amphoteric nature:** Water can act both as an acid as well as a base and is thus said to be an amphoteric substance.

   Water as base: Water acts as a base towards acids stronger than it as shown below,

   $$H_2O + HCl \longrightarrow H_3O^+ + Cl^-$$

   Water as an acid: Water acts as an acid towards bases stronger than it.

   $$H_2O + NH_3 \longrightarrow OH^- + NH_4^+$$

2. **Redox reactions involving water:** Water can act both as oxidising as well as reducing agent.

   Oxidising agent: Water acts as an oxidising agent when it gets reduced.

   $$2H_2O + 2Na \longrightarrow 2NaOH + H_2$$

   Reducing agent: Water acts as a reducing agent when it gets oxidised.

   $$2H_2O + 2F_2 \longrightarrow 4H^+ + 4F^- + O_2$$

3. **Hydrolysis reaction:** Water is an excellent solvent due to its high dielectric constant (78.39). In addition, water can easily hydrolyses many ionic and covalent compounds.

   Water hydrolyses oxides and halides of non-metals forming their respective acids

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

4. **Hydrates Formation:** From aqueous solutions many salts can be crystallised as hydrated salts. Hydrates are of three types:
   - **i. Coordinated water**

     For example: $[Ni(H_2O)_6]_{2+}\ (NO_{3-})_2$ and $[Fe(H_2O)_6]Cl_3$
   - **ii. Interstitial water**

     For example: $BaCl_2.2H_2O$
   - **iii. Hydrogen bonded water**

     For example: $[Cu(H_2O)_4]^{2+}\ SO_4^{2-}\ H_2O$ in $CuSO_4.5H_2O$

Hard and Soft Water

Hard water is the one which does not produce lather with soap easily due to the presence of calcium and magnesium salts in the form of their bicarbonates, chlorides and sulphates. For example, sea water etc.

Soft water is the one which is free from the soluble salts of calcium and magnesium. It gives lather with soap easily. For example, distilled water, rain water etc.

Types of Hardness

1. **Temporary hardness:** It is due to the presence of bicarbonates of calcium and magnesium. Temporary hardness is called so because it can be easily removed by boiling.
2. **Permanent hardness:** This type of hardness is due to the presence of chlorides and sulphates of calcium and magnesium dissolved in water. As this type of hardness cannot be removed by simple boiling, therefore it is known as permanent hardness.

Softening of Water

The process of removal of hardness from water is called softening of water.

i. **Removal of temporary hardness:** Temporary hardness can be removed by the following methods:

   a) **Boiling:** The temporary hardness of water can easily be removed by boiling the water in large boilers. During boiling the soluble $Mg(HCO_3)_2$ is converted into $Mg(OH)_2$ instead of $MgCO_3$ because $Mg(OH)_2$ is precipitated easily, whereas $Ca(HCO_3)_2$ is changed to insoluble $CaCO_3$ and gets precipitated. These precipitates can be removed by filtration process. So, the filtrate obtained will be soft water.

$$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 + 2CO_2$$

$$Ca(HCO_3)_2 \longrightarrow Ca(OH)_2 + H_2O + 2CO_2$$

   b) **Clark's method:** In this process the calculated amount of lime is added to hard water containing bicarbonates of calcium and magnesium. It precipitates out calcium carbonate and magnesium hydroxide which are then filtered to obtain soft water.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + Mg(OH)_2\downarrow + 2H_2O$$

ii. **Permanent hardness:** Permanent hardness of water is due to the presence of chlorides and sulphates of calcium and magnesium. It cannot be removed by simple boiling. So, the following methods are employed for removing permanent hardness:

   a) **Treatment with washing soda:** When calculated amount of Na_2CO_3 (washing soda) is added to hard water containing soluble sulphates and chlorides of calcium and magnesium, then these soluble salts get converted into insoluble carbonates which get precipitated.

$$CaCl_2 + Na_2CO_3 \longrightarrow 3CaCO_3\downarrow + 2NaCl$$

$$MgSO_4 + Na_2CO_3 \longrightarrow 3MgCO_3\downarrow + Na_2SO_4$$

d) **Ion-exchange method:** This process employs the use of zeolite or permutit which is hydrated sodium aluminium silicate ($NaAlSiO_4$), therefore, it is also known as zeolite/permutit process. For the sake of simplicity sodium aluminium silicate is written as NaZ. When zeolite is added to hard water, the cations present in hard water are exchanged for sodium ions.

$$2NaZ(s) + M^{2+}(aq) \longrightarrow MZ_2(s) + 2Na^{+}(aq)\ (M = Mg, Ca)$$

Hydrogen Peroxide

Hydrogen peroxide was discovered by a French chemist J. L. Thenard. It is an important chemical used in pollution control treatment of domestic and industrial effluents.

Preparation

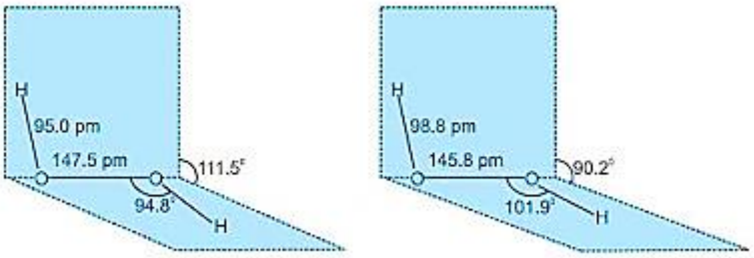
By the action of sulphuric acid on hydrated barium peroxide

$$BaO.8H_2O + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2 + H_2O$$

Physical Properties

1. Pure hydrogen peroxide is a syrupy liquid. It is colourless but gives a bluish tinge in thick layers.
2. It is soluble in water, alcohol and ether in all proportions.
3. It is more viscous than water. This is due to the fact that molecules of H_2O_2 are more associated through H-bonding.

Structure



(a) Gas phase (b) Solid phase

Chemical Properties

a) **Oxidising property:** Hydrogen peroxide acts as an oxidising agent both in acidic as well as in alkaline medium.

$$H_2O_2 + 2H^{+} + 2e^{-} \longrightarrow 2H_2O$$

b) **Reducing Property:** In presence of strong oxidising agents, hydrogen peroxide behaves as a reducing agent in both the medium.

$$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$

c) **Decomposition:** H2O2 is an unstable liquid

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Uses

1. In daily life it is used as a material to bleach delicate materials like hair, cotton, wool, silk etc.
2. It is used as a mild disinfectant. It is also a valuable antiseptic which is sold under the name of perhydrol.

3. In the manufacture of sodium perborate, sodium percarbonate. These are used in high quality detergents.
4. In the synthesis of hydroquinone, tartaric acid and certain food products and pharmaceuticals (cephalosporin) etc.
5. It is used in industries as a bleaching agent for paper pulp, leather, oils, fats and textiles etc.

Heavy Water (D_2O)

Method Heavy water is chemically deuterium oxide (D_2O). It was discovered by Urey in 1932.

Preparation

It is prepared by the exhaustive electrolysis of water. When prolonged electrolysis of water is done, then H_2 is liberated much faster than D_2 and the remaining water becomes enriched in heavy water.

$$H_2O + D_2 \longrightarrow D_2O + H_2$$

Uses

1. Heavy water is used as a moderator in nuclear reactors.
2. It is used as a tracer compound, in studying the reaction mechanisms.
3. It is used as a starting material for the preparation of a number of deuterium compounds.

Hydrogen Economy

One proposed way to meet the need for new energy sources is to burn hydrogen as a fuel in industry and power plants and possibly also in homes and motor. This proposal is referred to hydrogen economy.

Advantages of hydrogen economy

1) Dihydrogen releases large quantities of heat on combustion. The energy released by combustion of fuels like dihydrogen, methane, LPG as compared in terms of the same amount in mole, mass and volume. On mass to mass basis, dihydrogen can release more energy than gasoline i.e. Octane number is about 3 times.

Energy released on combustion (in KJ)	Dihydrogen (in gaseous state)	Dihydrogen (in liquid state)	LPG	CH_4 gas	Octane (in liquid state)
per mole	286	285	2220	880	5511
per gram	143	142	50	53	47
per litre	12	9968	25590	35	34005

2) Burning of hydrogen in air or dioxygen not only liberates large amount of energy but yields water as the only product. Burning of hydrogen produces no pollutant like SO2 that are responsible for acid rain ,nor carbon dioxide that is responsible for the greenhouse effect ,nor carcinogenic hydrocarbons nor lead compounds.

There are two major barriers in achieving the goal of hydrogen economy

1) To find out a cheap method for large scale production of dihydrogen.

Two methods which have been proposed are:

a) Electrolysis of water and the thermochemical reactions cycle. The first method is not economically viable since the cost of production of dihydrogen by electrolysis of water is so high that almost all dihydrogen is obtained from natural gas which itself is in short supply.

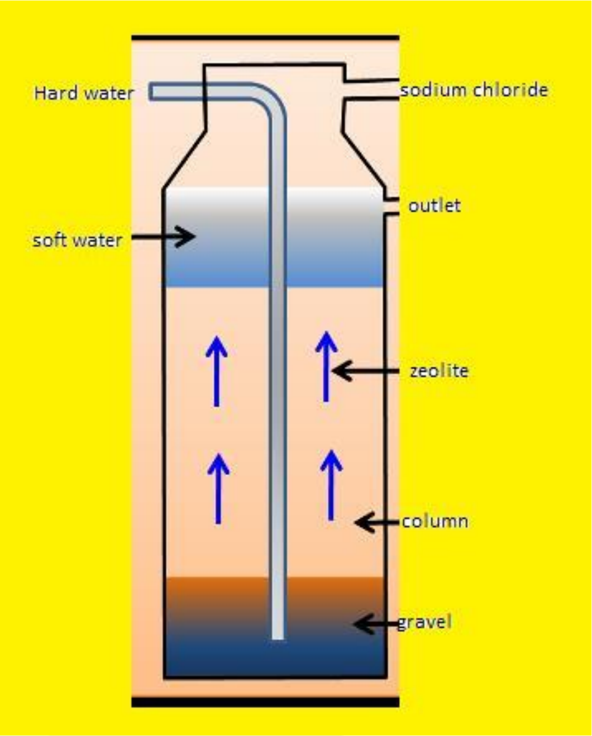
b) The other method involves series of thermochemical reactions in which the only things consumed are water and heat and only products are hydrogen and oxygen while all the other species are recycled.

2) To find out an effective means of storing dihydrogen.

The gaseous dihydrogen because of its bulk, is difficult to store, but liquid dihydrogen can be stored relatively easily and safely in cryogenic tanks.

It is also feasible to transport liquid dihydrogen by road or rail tankers of 20000 US gallons capacity. It can also be stored in underground tanks and transported by pipelines. However, it may not be convenient to store liquid dihydrogen in a home or in a car since the boiling point of dihydrogen is very low.

Dihydrogen must be kept out of contact with oxygen or air with which it forms explosive mixture. The only alternative left is to store dihydrogen or metal in an alloy as interstitial hydride.



Methods to remove hardness

Temporary hardness: It can be removed by following methods:

- Boiling
- Clarks method

Boiling: In this when we boil hard water, bicarbonates are convereted into hydroxides and calcium bicarbonate is converted into carbonates. These precipitates are filtered and thus, hardness is removed.

Clark's method: In this method calculated amount of lime is added that precipitates Calcium and Magnessium carbonates.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$$

Calcium bicarbonate Calcium hydroxides Calcium carbonate water

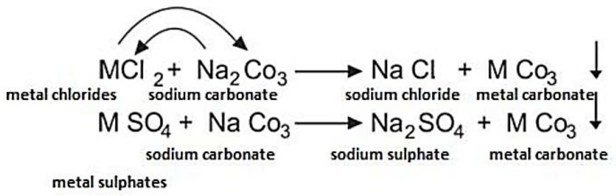
$$Mg(HCO_3)_2 \quad + \quad Ca(OH)_2 \quad \longrightarrow \quad CaCO_3 \quad + \quad H_2O \quad + \quad Mg(OH)_2$$

Magnesium bicarbonate Calcium hydroxides Calcium carbonate magnesium hydroxide

Permanent hardness: It is removed by following methods:

- With washing soda
- Calgon's process
- Ion exchange method
- Synthetic resin method

1. **With washing soda:** In this washing soda is added. It reacts with calcium and magnessium chlorides and sulphates to form soluble carbonates as shown:



Ion – exchange method

In this a substance called zeolite or permutit is added. This zeolite exchange Sodium with Calcium and Magnessium ions of hard water.

Example of permutit is many like: hydrated Sodium Aluminium Silicates ($Na_2Al_2Si_2O_8.xH_2O$) commonly can be indicated as NaZ.

The apparatus is set as shown:

Procedure:

- The zeolite is loosely packed over layers of gravel and sand in big tank.
- Hard water is introduced from top into the base of tank.
- From the bottom water rises up through gravel and sand layers.
- Finally, it percolates through the bed of permutit.
- During this the ions are exchanged.
- So, the water above the permutit layer is generally soft water.

$$Mg^{2+} + Na\ Z\ ----- \quad MgZ_2 + 2Na^{+}$$

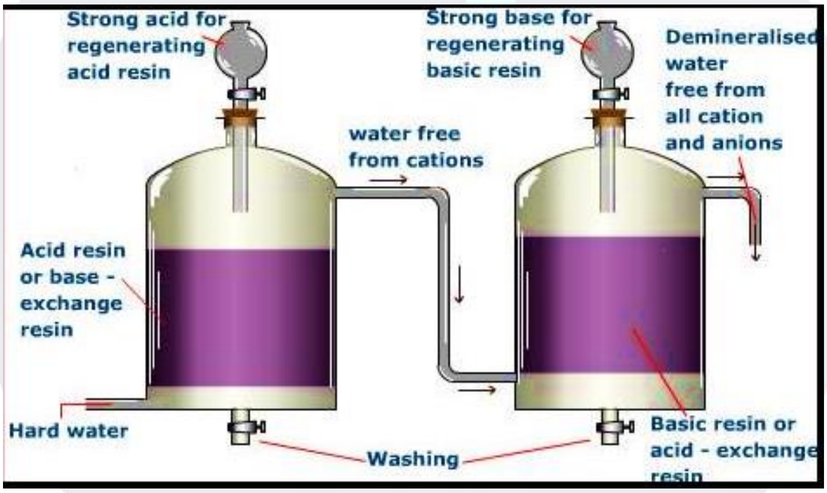
Magnesium ion Zeolite ion exchanged

$$Ca^{2+} + Na\ Z\ ----- \quad CaZ_2 + 2Na^{+}$$

Calcium ion zeolite ion exchanged

3. Synthetic Resin Method

Synthetic resin methods are more superior than the ion exchange method as they remove all types of cations and anions and the resultant water is distilled water.



These resins are generally of two types:

- Cation exchange resin
- Anion exchange resin

Cation exchange resin: It consist of giant hydrocarbon framework attached to basic groups. They are represented by general formula R-COOH or R-SO_3H. In this R is giant hydrocarbon. These resins can exchange H^+ ions with cations present in hard water.

Anion exchange resin: It consist of giant hydrocarbon framework attached to basic groups like OH- ions, usually in the form of substituted ammonium hydroxides. They are represented as R-NH_3OH- where R denotes giant hydrocarbon framework. These resins can exchange hydroxide ion with anions like chloride ions and sulfate ions present in hard water.

$$R-COO^{-}H^{+} + CaCl_2 \longrightarrow (RCOO)_2\,Ca + 2H^{+} + 2Cl^{-}$$

Carboxylic acid calcium chloride calcium salt of carboxylic acid chloride ion

Thus, the water that comes out from the tank is richer in hydrogen ions, this water is then passed through second tank, here the anions are exchanges with hydroxide ion to form distilled water.

$$R-NH_3OH+SO_4^{2-}\longrightarrow(R-NH_3)_2\,SO_4^{2-}+2OH^-$$

Sulphate ions hydroxide ions

$$H^++OH^-\longrightarrow H_2O$$

Hydrogen ion hydroxide ion water

4. **Calgon process**

In this procss calcium and magnessium ions are rendered ineffective by treatment with sodium polymetaphosphate . The trade name for it is Calgon. when Calgon is added to hard water the Calcium, Magnessium ions present in it combine with this Calgon to form soluble complex of Calcium and Magnessium salts .

That is:

$$CaCl_2 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Ca_2(PO_3)_6 + NaCl]$$

Calcium chloride (Calgon) Soluble salt of calcium salt Sodium chloride

Summary-

1. Hydrogen has the simplest atomic structure with only one proton and one electron. It is the only element which has no neutron.
2. Hydrogen has properties similar to both alkali metals as well as halogens. Therefore, its position in the periodic table was not certain and it is best placed separately.
3. There are three isotopes of hydrogen namely protium ($_1H^1$), deuterium ($_1H^2$, D) and tritium ($_1H^3$, T) . The predominant form of hydrogen is protium which has no neutron, deuterium has one neutron, tritium which is radioactive has two neutrons.
4. Hydrogen in its elemental form exists as dihydrogen. Dihydrogen is the most abundant element in the universe.
5. ‘Syn gas’ or ‘water gas’ is a mixture of CO and H_2.
6. Dihydrogen is colourless, odourless and combustible gas. The H–H bond dissociation enthalpy is the highest for a single bond between two atoms of any element.
7. The main use of dihydrogen is in the formation of vegetable ghee by hydrogenation of vegetable oils and also the formation of ammonia by Haber’s process.
8. Atomic hydrogen and oxyhydrogen torches are used for cutting and welding purpose.
9. It acts as a rocket fuel and even has a promising potential for use as a non-polluting fuel of the near future (hydrogen economy).
10. Hydrogen forms three category of hydrides namely ionic hydrides, covalent hydrides and metallic hydrides.
11. Covalent hydrides are further classified into electron-deficient, electron-precise and electronrich hydrides based on the relative number of electrons and bonds in their Lewis structures.
12. Water is a substance which is of great chemical and biological significance. It is a solvent of great importance.
13. Water has highest density at 4°C.
14. Water reacts with large number of substances. It exhibits amphoteric nature.
15. Water dissolves many salts in it making it hard. Hard water is the one which contains calcium and magnesium salts in the form of hydrogencarbonate, chlorides and sulphates.
16. The temporary hardness of water is due to the presence of magnesium and calcium hydrogencarbonates which can be removed simply by boiling.
17. The permanent hardness of water is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates. It is mainly removed by the ion-exchange methods.
18. Hydrogen peroxide has a non-planar open-book like structure. It is a good bleaching agent and is used in pollution control treatment of industrial and domestic effluents.

Class : 11th Chemistry
Chapter- 9: Hydrogen

Hydrogen

Dihydrogen (H_2)

Occurrence: Most abundant in universe.

Preparation:

– Laboratory Method:

- $Zn+2H^+ \rightarrow Zn^{2+}+H_2$
- $Zn+2NaOH \rightarrow Na_2ZnO_2+H_2$

–Commercial Method:

- $2H_2O(l) \xrightarrow[\text{Traces of acid/base}]{\text{Electrolysis}} 2H_2(g)+O_2(g)$
- By electrolysing warm aqueous barium hydroxide solution between Nl electrodes.
- $C_nH_{2n+2}+nH_2O \xrightarrow[\text{Ni}]{1270\text{ K}} nCO+(2n+1)H_2$

–$CO+H_2$ is called water gas

–Cool Gasification : $C(s)+H2O(g) \xrightarrow{1270\text{ K}} CO_{(g)}+H_{2(g)}$

–Water-gas shift reaction : $CO(g)+H_2O_{(g)} \xrightarrow[\text{Catalyst}]{673\text{ K}} CO_{2(g)}+H_{2(g)}$

Physical Properties:

- Colourlers, odourless, tasteless and combustible.
- Lighter than air, insoluble in water.

Chemical Properties:

$H_{2(g)}+X_{2(g)} \longrightarrow 2HX_{(g)}$ (X=F, Cl,Br,I)

$2H_{2(g)}+O_{2(g)} \xrightarrow[\text{Heating}]{\text{Catalyst or}} 2H_2O(l)\ \Delta H^\circ=-285.9\ \text{KJmol}^{-1}$

$3H_{2(g)}+N_{2(g)} \xrightarrow[\text{Fe}]{673\text{ K, }200\text{ atm}} 2NH_{3(g)}\ \Delta H^\circ=-92.6\ \text{KJmol}^{-1}$

$H_{2(g)}+2M_{(g)} \longrightarrow 2MH_{3(s)}$ Where M= alkali metal

$H_{2(g)}+Pd^{2+}_{(aq)} \longrightarrow Pd_{(s)}+2H^+_{(aq)}$

$H_2+CO+RCH=CH_2 \longrightarrow RCH_2CH_2CHO$

$H_2+RCH_2CH_2CHO \longrightarrow RCH_2CH_2CH_2OH$

Uses:

- Synthesis of ammonia.
- In manufacture of vanaspati fat.
- In manufacture of bulk organic chemicals.
- For manufacture of metal hydrides
- Preparation of HCl.
- In metallurgical processes.
- As a rocket fuel
- In fuel cells

Heavy Water (D_2O)

Preparation: By exhaustive electrolysis of water.

Uses:

- As a moderator in nuclear reactors.
- In exchange reactions for the study of reaction mechanisms.

Isotopes

Protium: Predominant form.(^1_1H)

Deuterium: (^2_1H)

Tritium : Radioactive (^3_1H)

Properties

- Resembles alkali metals (lose one e- to form unipositive ions).
- Resembles halogens (gain one e- to form uninegative ion).
- Forms oxides, halides and sulphides.
- Very high ionization enthalpy.
- Does not possess metallic characters under normal conditions.
- Forms diatomic molecules

Hydrides

Types:

(i). Ionic/saline/saltlike: Stoichiometric compounds of dihydrogen formed with s-block elements.

(ii). Covalent/molecular: Formation of molecular compounds from dihydrogen and p-block elements.

(iii). Metallic/non-stoichiometric/interstitial: Formed by d-block and f-block elements.

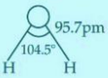
Water

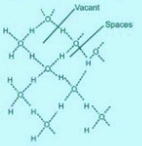
(Human body: 65%, Plants: 95%)

Physical Properties:

- Colourless and tasteless
- Presence of extensive H bonding.
- High freezing point, high B.P., high heat of vaporization, high heat of fusion

Structure:





Chemical Properties:

$H_2O_{(l)}+NH_{3(aq)} \rightleftharpoons OH^-_{(aq)}+NH_4^+{}_{(aq)}$

$2H_2O_{(l)}+2Na_{(s)} \longrightarrow 2NaOH_{(aq)}+H_{2(g)}$

$6CO_{2(g)}+12H_2O_{(l)} \longrightarrow C_6H_{12}O_{6(aq)}+6H_2O_{(l)}+6O_{2(g)}$

$P_4O_{10(s)}+6H_2O_{(l)} \longrightarrow 4H_3PO_{4(aq)}$

Difference: Hard water does not give lather with soap whereas soft water gives lather easily. Temporary hardness: Removed by boiling, Clark's method. (Due to presence of magnesium and calcium hydrogen carbonates)

Permanent hardness: Removed by treatment with washing soda, Calgon's method, Ion exchange method, synthetic resins methods. (Due to presence of soluble salts of Mg and Ca in the form of chlorides and sulphate)

Electronic Configuration

$1S^1$

Hydrogen Peroxide (H_2O_2)

Preparation

- $BaO_2 .8H_2O_{(s)}+H_2SO_{4(aq)} \rightarrow BaSO_{4(s)}+H_2O_{2(aq)}+8H_2O_{(l)}$
- $2HSO^-_{4(aq)} \xrightarrow{\text{Electrolysis}} HO_2SOOSO_3H_{(aq)} \longrightarrow 2HSO^-_{4(aq)}+2H^+_{(aq)}+H_2O_{2(aq)}$
- 2– ethylanthraquinol $\underset{H_2/Pd}{\overset{O_2(air)}{\rightleftarrows}}$ H_2O_2+ Oxidised Product

Physical Properties

- Colourless, miscible with water.

Structure: Non-Planar

Chemical Properties:

$PbSO_{4(s)}+4H_2O_{2(aq)} \rightarrow PbSO_{4(s)}+4H_2O_{(l)}$

$HOCl+H_2O_2 \rightarrow H_3O^++Cl+O_2$

$Mn^{2+}+H_2O_2 \rightarrow Mn^{4+}+2OH^-$

$I_2+H_2O_2+2OH^- \rightarrow 2I^-+2H_2O+O_2$

Decomposes on exposure

Uses

- As hair bleach, disinfectant.
- Manufacture chemicals used in detergents.
- In industries as bleaching agent.
- In environmental chemistry.

Important Questions

Multiple Choice questions-

1. When water is dropped over sodium peroxide, the colourless gas produced is:

(a) Di-Nitrogen
(b) Di-Oxygen
(c) Di-Hydrogen
(d) Hydrogen Peroxide

2. The atomic weights of isotopes of all element are different due to different number of ________.

(a) Protons
(b) Electrons
(c) Neutrons
(d) None of Above

3. During the reaction of natural gas and steam the catalyst used is

(a) Fe
(b) Zn
(c) Ni
(d) Cr

4. Cavendish in 766 discovered.

(a) Nitrogen
(b) Oxygen
(c) Hydrogen
(d) Helium

5. Dihydrogen gas may be prepared by heating caustic soda on

(a) Cu (b) Zn
(c) Na (d) Ag

6. Hydrogen set free at the time of its preparation from its compound in atomic form are called ________.

(a) Nascent Molecular Hydrogen
(b) Nascent Atomic Hydride
(c) Both (1) and (2)
(d) Nascent Hydrogen

7. Which substance does not speed up decomposition of H_2O_2

(a) Glycerol
(b) Pt
(c) Gold
(d) MnO_2

8. Water shows anomalous behavior between

(a) 0 to 4 °C
(b) 0 to 5 °C
(c) 0 to -4 °C
(d) 4 to 0 °C

9. Which of the following pair of substance will not evolve H_2 gas?

(a) Iron and aqueous H_2SO_4
(b) Copper and HCl(aq)
(c) Sodium and Ethanol
(d) Iron and Steam

10. Tritium ________ radioactive isotope.

(a) Beta-Emitting
(b) Alpha – Emitting
(c) Gamma-Emitting
(d) None of the Above

11. The maximum density of water at 40C is:

(a) $1.0\ g / cm^3$
(b) $0.998\ g / cm^3$
(c) $0.918\ g / cm^3$
(d) $1.2\ g / dm^3$

12. Water gas is mixture of hydrogen H_2 and

(a) CO
(b) CO_2
(c) Cl_2
(d) SO_2

13. The volume of oxygen gas evolved at STP by decomposition of 0.68 g "20 volume" hydrogen peroxide is:

(a) 112 ml
(b) 224 ml
(c) 56 ml
(d) 336 ml

14. Which of the following statements regarding hydrogen peroxide is/are incorrect?

(a) As aerating agent in production of sponge rubber
(b) As an antichlor
(c) For restoring white colour of blackened lead painting
(d) All of the above

15. ______ on water decolourises H_2O_2

    (a) O_3

    (b) Acidic $KMnO_4$ solution

    (c) Black Suspension of Lead Sulphide (PbS)

    (d) None of these

Very Short:

1. Which gaseous compound on treatment with dihydrogen produces methanol?
2. What are the constituents of water gas?
3. Arrange H_2, D_2, T_2 in the decreasing order of them
   (i) Boiling point
   (ii) Heat of fusion.
4. Which isotope of hydrogen
   (i) does not contain neutron
   (ii) is radioactive?
5. Out of the following metals which can be used to liberate H_2 gas on reaction with dil. hydrochloric acid?
   (i) Cu,
   (ii) Zn,
   (iii) Iron,
   (iv) Silver,
   (v) Magnesium
6. Name one compound each of hydrogen in which it exists in:
   (i) Positive oxidation state
   (ii) Negative oxidation state.
7. What is the importance of heavy water in nuclear power generation?
8. State two properties in which hydrogen resembles alkali metals.
9. Give an example of each anionic and covalent hydride.
10. Why is H_2O_2 concentrated at low pressure?

Short Questions:

1. Hydrogen forms three types of bonds in its compounds. Describe each type of bonding using suitable examples.
2. Name one example of a reaction in which dihydrogen acts as
   (i) an oxidizing agent
   (ii) a reducing agent.
3. The process $\frac{1}{2} H_2(g) + e^- \rightarrow H^-(g)$ is endothermic (DH = +151 kJ mol^{-1}), yet salt- like hydrides are known. How do your account for this?
4. Find the volume strength of 1.6 N H_2O_2 solution.
5. A sample of hard water is allowed to pass through an anion exchanger. Will it produce lather with soap easily?
6. Anhydrous BaO_2 is not used for preparing H_2O_2 Why?

Long Questions:

1. (a) Compare atomic hydrogen with nascent hydrogen.
   (b) What is (i) active hydrogen
   (ii) heavy hydrogen? How are they formed?
2. How is the solution of H_2O_2 concentrated?
3. What are the different methods used for the softening of hard water? Explain the principle of each method.
4. Show how hydrogen peroxide can function both as an oxidising and a reducing agent
5. Calculate the percentage strength & strength in g/L of 10 volume hydrogen peroxide solution.

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): Permanent hardness of water is removed by treatment with washing soda.

   Reason (R): Washing soda reacts with soluble magnesium and calcium sulphate to form insoluble carbonates.

   (i) Statements A and R both are correct and R is the correct explanation of A.
   (ii) A is correct but R is not correct.
   (iii) A and R both are correct but R is not the correct explanation of A.
   (iv) A and R both are false.

2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): Some metals like platinum and palladium, can be used as storage media for hydrogen.

   Reason (R): Platinum and palladium can absorb large volumes of hydrogen.

(i) Statements A and R both are correct and R is the correct explanation of A.
(ii) A is correct but R is not correct.
(iii) A and R both are correct but R is not the correct explanation of A.
(iv) A and R both are false.

Case Study Based Question:

1. Read the passage given below and answer the following questions:

Hydrogen can exist in three isotopic forms, viz., protium, deuterium and tritium, which differ from each other in the number of neutrons.

Out of these three isotopes, tritium is formed in the upper atmosphere by reaction induce by cosmic rays. It decays to emit low energy β-particles.

$$^{3}_{1}H \longrightarrow {}^{3}_{2}He + {}_{-1}e^{0}$$

Tritium β-particle

Tritium is used for making thermonuclear devices and for carrying out researches in fusion reactions as a source of energy. It is also used as a radioactive tracer as it is relatively cheap and easy to work with.

(1) The relative atomic mass of isotopes of hydrogen is:
(a) 1 : 2 : 3
(b) 1 : 1 : 2
(c) 2 : 4 : 5
(d) 1 : 2 : 4

(2) The n/ p ratio for $_1H^2$ is:
(a) 1 : 2
(b) 1 : 1
(c) 2 : 1
(d) 2 : 3

(3) Which is the most reactive isotope of hydrogen?
(a) Tritium
(b) Deuterium
(c) Protium
(d) All are equally reactive

(4) What type of reactions are generated by tritium?
(a) Chemical reaction
(b) Radioactive reaction
(c) Addition reaction
(d) All of these

2. Read the passage given below and answer the following questions:

Water is the main constituent of earth's hydrosphere and fluids of all known living organisms. It is vital for all known forms of life, even though it provides no chlorines or organic nutrients.

Water cover approximately 70.9% of earth's surface, mostly in seas and oceans. Water plays an important role in the world economy. Approximately 70% of the fresh water used by humans goes to agriculture. Water is the excellent solvent for a wide variety of substance both mineral and organic; as such it is widely used in industrial processes and in cooking and washing. Water, ice and snow are also central to many sports and other forms of entertainment pure water has a low electrical conductivity, which increases with the dissolution of a small amount of ionic material such as common salt.

(1) Which one of the following statements about water is incorrect?
(a) Water can act both as an acid and as a base
(b) Water can be easily reduced to dihydrogen by highly electronegative elements.
(c) Ice formed by heavy water sinks in normal water
(d) Presence of water can be detected by adding a drop to anhydrous $CuSO_4$

(2) In nuclear reactors, ordinary water is not used as a moderator because
(a) it cannot slow down the fast-moving neutrons
(b) it cannot remove the heat from the reactor core
(c) it has corrosive action on the metallic parts of the nuclear reactor
(d) None of the above

(3) Consider the following statements about intermolecular and intramolecular hydrogen bonding.
I. Both types of H-bonds are temperature dependent.

II. Water exhibits amphoteric nature.

III. The boiling points of compounds having intramolecular H-bond are lower than those having intermolecular H-bond.

Which of the statements given above are correct?

(a) I and III

(b) Both II and III

(c) I and II

(d) All of these

(4) Consider the following statements regarding water.

There is extensive hydrogen bonding between water molecules.

I. Water has high melting point in comparison to H_2S and H_2Se.

II. High heat of vaporisation and heat capacity of water are responsible for moderation of climate and body temperature of living beings.

III. Covalent compounds like alcohol and carbohydrates dissolve in water.

Select the correct statements among above.

(a) Both I and II

(b) Both II and IV

(c) I, II and III

(d) All of these

Answer Key

MCQ

1. (b) DiOxygen
2. (c) Neutrons
3. (c) Ni
4. (c) Hydrogen
5. (b) Zn
6. (a) Nascent Molecular Hydrogen
7. (b) Pt
8. (a) 0 to 4 °C
9. (b) Copper and HCl(aq)
10. (a) Beta-Emitting
11. (a) 1.0 g / cm^3
12. (a) CO
13. (b) 224 ml
14. (d) All of the above
15. (c) Black Suspension of Lead Sulphide (PbS)

Very Short Answer:

1. Carbon monoxide (CO).
2. Carbon monoxide and hydrogen.
3. T2 > D2 > H2 T2 > D2 > H2.
4. Protium

   Tritium.
5. Only Zn, Fe, Mg.
6. HCl

   NaH.
7. It is used as a moderator in nuclear reactions to slow down the speed of fast-moving neutrons.
8. Both form unipositive ion

   Both have one electron in their s orbital (ns1).
9. Ionic Hydride NaH Covalent hydride NH_3.
10. Because it decomposes at ordinary pressure or on heating.

Short Answer:

1. Ans: Hydrogen forms compounds in three different ways:

1. By loss of electrons as in the reactions of H_2 with CuO

$$CuO(s)+H_2O \xrightarrow{Heat} Cu(s)+ \underset{[Hydrogen\,bonding]}{H_2O(g)}$$

2. By gain of electrons as in reactions of H_2 with metals.

$$Na(s)+H_2(g) \xrightarrow{Heat} \underset{[Ionic\ bonding]}{2NaH(s)}$$

$$Ca(s)+H_2(g) \xrightarrow{Heat} CaH_2$$

3. By sharing of electrons as in the reactions of H_2 with halogens

$$H_2(g)+F_2(g)\longrightarrow \underset{[Covalent\ bonding]}{2H-F(l)}$$

$$H_2(g)+Cl_2(g)\longrightarrow 2H-Cl(g)$$

2. **Ans:** As an oxidizing agent

$$2Na(s)+H_2(g)\xrightarrow{Heat}2Na^{+}H^{-}(s)$$

Here Na has been oxidized to Na while dihydrogen has been reduced to H^+ ion.

(ii) a reducing agent.

$$CuO(s)+H_2(g)\xrightarrow{Heat}Cu(s)+H_2O(g)$$

Here CuO has been reduced to copper and H_2 has been oxidized to H_2O.

3. **Ans:** This is due to the reason that high lattice energy released (energy released during the formation of solid metal hydride from their corresponding gaseous ions, i.e., M^+ and H^+) more than compensates the energy, needed for the formation of H– ions from H_2 gas.

4. **Ans:** Strength = Normality × EQuestion wt.

Eq. wt.of H_2O_2 = 17

∴ Strength of 1.6N H_2O_2 solution = 1.6 × 17g L^{-1}

Now 68g of H_2O_2 gives 22400 mL O_2 at NTP/STP

∴ 1.6 × 17g of H_2O_2 will give = $\frac{22400}{68}$ × 1.6 × 17

= 8960 mL of O_2 at STP

But 1.6 × 17g of H_2O_2 are present in 1000 mL of H_2O_2 solution

Hence 1000 mL of H_2O_2 solution gives 8960 mL of O_2 at STP 1 mL of H_2O_2 will give = 8.96 mL of O_2 at STP.

Hence the volume strength of 1.6N H_2O_2 solution is = 8.96 volume

5. **Ans:** No. Ca^{2+} and Mg^{2+} ions are still present, and these will react with soap to form curdy white ppt. Therefore, it will not produce lather with soap solution easily.

6. **Ans:** $BaSO_4$ formed during the reaction of BaO_2 with H_2SO_4 forms a protective layer around unreacted BaO_2 and the reaction stops after some time.

Long Answer:

1. **Ans:** Comparison of atomic and nascent hydrogen

The main point of differences is:

1. Nascent hydrogen can be produced even at room temperature, but atomic hydrogen is produced only at very high temperature.
2. Nascent hydrogen can never be isolated, but atomic hydrogen can be isolated.
3. The reducing power of atomic hydrogen is much greater than that of nascent hydrogen.

In general reactivity of the three forms of hydrogen increases in order. Molecular hydrogen (H_2) < Nascent hydrogen < Atomic hydrogen.

Active Hydrogen: It is obtained by subjecting a stream of molecular hydrogen at ordinary temperature to silent electric discharge at about 30,000 volts. It is very reactive in nature (half-life = 0.33 second, and combines directly at ordinary temperatures with Pb and S forming their hydrides

Heavy hydrogen: It is manufactured by the electrolysis of heavy water containing a little of IT SO, or NaOH to make the solution conducting.

$$\underset{Heavy\ water}{3D_2O(l)}\longrightarrow \underset{at\ cathode}{2D_2(g)}+\underset{at\ anode}{O_2(g)}$$

In the laboratory, it can be prepared by the action of heavy water on sodium metal.

$$2D_2O(l) + 2Na(s) \rightarrow 2NaOD(aq) + D_2(g).$$

2. **Ans:** The concentration of hydrogen peroxide: Hydrogen peroxide obtained by any method is always in the form of a dilute solution. Great care is to be taken for concentrating its solution because it is unstable and decomposes on heating.

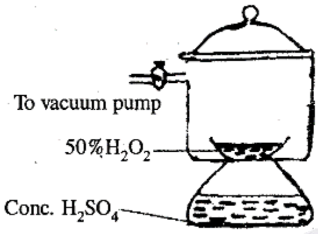
$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The decomposition of H_2O_2 is catalysed by the ions of heavy metals present as impurities.

The solution of H_2O_2 is concentrated by the following methods.

1. **By careful evaporation on a water bath:** A dilute solution of H_2O_2 is taken in a shallow evaporating dish and is heated at 313K – 323 K. Water evaporates slowly and a hydrogen-peroxide solution of about 15 – 50% strength is obtained.

2. **By dehydration in a vacuum desiccator:** The dilute (50 %) solution of H_2O_2 obtained as above, is further concentrated by placing the same in a vacuum desiccator containing concentrated H_2SO_4 as a dehydrating agent. Here, water vapours are absorbed by concentrated sulphuric acid. This is shown in the diagram



(Concentration of H_2O_2 in vacuum desiccator)

3. **By distillation under reduced pressure:** The solution of hydrogen peroxide is further concentrated by subjecting it to distillation under reduced pressure. The solution is distilled at 308 – 313 K under a reduced pressure of 15 mm Hg. Water present in the solution distils over leaving behind about 98 – 99% concentrated solution of hydrogen peroxide.
4. **By crystallization:** The last traces of water present in H_2O are removed by freezing it in a freezing mixture of solid CO_2 and others. The crystals of hydrogen peroxide separate out. These crystals are removed, dried and then remitted to obtain 100% pure hydrogen peroxide.
5. **Storage of hydrogen peroxide:** In order to check the decomposition of hydrogen peroxide, a small amount of acetanilide (i.e., negative catalyst) is added to it before storing the hydrogen peroxide.

Hydrogen peroxide cannot be concentrated by distillation at ordinary pressure because it undergoes decomposition into water and oxygen as it is a highly unstable liquid. It decomposes even on long-standing or on heating.

3. **Ans:** Hard water can be softened by the following methods depending upon the nature of hardness.

(a) Temporary hardness:

1. ***By boiling:*** It can be removed by merely boiling the water. Boiling decomposes the bicarbonates to give carbon dioxide and insoluble carbonates, which can be removed by filtration.

$$Ca(HCO_3)_2 \xrightarrow{Heat} \underset{white\,ppt.}{CaCO_3} + H_2O + CO_2$$

$$Mg(HCO_3)_2 \xrightarrow{Heat} \underset{white\,ppt.}{MgCO_3} + H_2O + CO_2$$

2. ***Clark's process:*** Temporary hardness can be removed by the addition of a calculated amount of lime, whereupon magnesium and/or calcium carbonates is precipitated.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO3_3 + MgCO_3 + 2H_2O$$

(b) Permanent hardness:

1. ***With sodium carbonate:*** On treatment with washing soda, Ca^{2+} and Mg^{2+} in hard water are precipitated. The precipitate of the insoluble carbonates thus formed is removed by filtration.

$$Ca^{2+} + CO_3^{2-} \longrightarrow \underset{white\ ppt.}{CaCO_3}$$

$$Mg^{2+} + CO_3^{2-} \longrightarrow MgCO_3$$

2. ***Ion-exchange method:*** The common substance used for this process is zeolite which is hydrated sodium aluminum silicate, $NaAl(SiO)_2$, The exchange occurs when passing over the zeolite bed, sodium ions from zeolite are replaced by calcium and magnesium ions. Thus

$$Na(Ze) + Mg^{2+} \rightarrow (Ze)_2Ca + 2Na^+$$

$$2NaZe + Mg^{2+} \rightarrow (Ze)_2Mg + 2Na^+$$

when all the sodium ions of the zeolite have been replaced, the zeolite is said to be exhausted. It can be regenerated by treatment with a strong solution of sodium chloride.

$$2Na + (Ze)_2Ca \rightarrow 2ZeNa + Ca^{2+}.$$

4. **Ans:** Oxidising properties: H_2O_2 has a tendency to accept electrons in chemical reactions and thus behaves as an oxidising agent in both acidic and alkaline medium.

$$H_2O_2 \rightarrow H_2O + O$$

In acidic medium

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$

In alkaline medium

$$H_2O_2 + OH^- + 2e^- \rightarrow 3OH^-$$

Example:

(a) In acidic medium:

$$2Fe^{2+} + 2H^+ + H_2O_2 \rightarrow 2Fe^{3+} + 2H_2O$$

(b) In alkaline medium:

$$3Cr^{3+} + 4H_2O_2 + 10OH^- \rightarrow 3CrO_4^{2-} + 8H_2O$$

Reducing properties: H_2O_2 can give electrons in a few reactions and thus behaves as a reducing agent.

In acidic medium

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$$

In alkaline medium

$$H_2O_2 + 2OH^- \rightarrow 2H_2O + O_2 + 2e^-$$

Reducing property in acidic medium:

$$2MnO_4^{2-} + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

Reducing property in basic medium:

$$2Fe^{3+} + H_2O_2 + 2OH^- \rightarrow 2Fe^{2+} + O_2 + 2H_2O$$

5. Ans: H_2O_2 decomposes on heating according to the equation

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

2× 34 g 22.4 L at N.T.P.

or 22400 cm³ at N.T.P.

From the equation

22.4L of O_2 at N.T.P are obtained from 68g of H_2O_2

∴ 10 ml of O_2 at N.T.P will be obtained from $\frac{68}{22400} \times 10$g of H_2O_2

But 10 ml of O_2 at N.T.P are produced from 1 ml. of 10 volume H_2O_2 solution.

Thus 1 ml of 10 volume H_2O_2 solution contains $\frac{68}{22400} \times 10$ g of H_2O_2

∴ 100 ml. of 10 volume H_2O_2 solution will contain

$$\frac{68}{22400} \times \frac{10}{1} \times 100 = 3.036\text{g.}$$

Thus a 10 volume H_2O_2 solution is approx. 3%

Alternatively, 1000 ml of 10 volume of H_2O_2will contain H_2O_2

$$\frac{68}{22400} \times 10 \times 1000 = 30.36\text{g}$$

Therefore, strength of H_2O_2 in 10 volume H_2O_2 is 30.36 g/L

Assertion Reason Answer:

1. (i) Statements A and R both are correct and R is the correct explanation of A.
2. (i) Statements A and R both are correct and R is the correct explanation of A.

Case Study Answer:

1. Answer:

(1) (a) 1 : 2 : 3

(2) (b) 1 : 1

(3) (a) Tritium

(4) (b) Radioactive reaction

2. Answer:

(1) (b) Water can be easily reduced to dihydrogen by highly electronegative elements.

(2) (d) None of the above

(3) (d) All of these

(4) (c) I, II and III

❖❖

The S-Block Elements

10

Introduction

In the previous chapter we have discussed about The Hydrogen but in this chapter we will study the general characteristics of the alkali and alkaline earth metals and their compounds. We will also study the compounds of s-block elements, their uses and importance, commercially and industrially. The biological significance of sodium, potassium, calcium and magnesium will also be discussed in this chapter.

The s-Block Elements

The s-block elements of the Periodic Table are those in which the last electron enters the outermost s-orbital. As the s-orbital can accommodate only two electrons, two groups (1 & 2) belong to the s-block of the Periodic Table.

Group-1 of periodic table contains

Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Caesium (Cs) and Francium (Fr). Together these elements are called alkali metals because they form hydroxides on reaction with water, which are strongly alkaline in nature.

The group-2

Includes Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra). Except Beryllium, rest of the elements of group-2 are called the alkaline earth metals. These are called so because their oxides and hydroxides are alkaline in nature and these metal oxides are found in the earth crust.

Group-1 Elements: Alkali Metals

1. Electronic Configuration

Electronic Configuration of elements of group-1 is ns^1, where n represents the valence shell. The alkali metals have one valence electron, outside the noble gas core.

Element	Symbol	Electronic configuration
Lithium	Li	$1s^22s^1$
Sodium	Na	$1s^22s^22p^63s^1$
Potassium	K	$1s^22s^22p^63s^24s^1$
Rubidium	Rb	$1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^1$
Caesium	Cs	$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^66s^1$ or $[Xe]\ 6s^1$
Francium	Fr	$[Rn]7s^1$

2. Atomic and ionic radii

The atoms of alkali metals have the largest size in their respective periods. The atomic radius increases on moving down the group because on moving down the group there is a progressive addition of new energy shells.

3. Ionization enthalpy

The ionization enthalpies of the alkali metals are generally low and decrease down the group from Li to Cs. This is because on moving down the group is due to increase in size of the atoms of alkali metals and increase in the magnitude of screening effect.

4. **Hydration enthalpy**

The alkali metal ions are extensively hydrated in aqueous solutions. The hydration enthalpies of alkali metal ions decrease with increase in ionic size $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$.

5. **Physical properties**

i. Alkali metals are silvery white in colour and are generally soft and light metals.

ii. The densities of alkali metals are low and increase down the group. Alkali metals have low melting and boiling point.

iii. When alkali are heated metals they impart characteristic colours to the flame.

iv. When the excited electron comes back to the ground state, there is emission of radiation in the visible region.

6. **Chemical Properties**

The alkali metals are highly reactive elements. The cause for their high chemical reactivity is:

i. Low value of first ionisation enthalpy

ii. Large size

iii. low heat of atomisation.

i. **Reaction with Air:** Alkali metals burn very fast in oxygen and form different kind of oxides like monoxides, peroxides and superoxides. In all the compounds formed by alkali metals with oxygen, their oxidation state is +1.

$$4Li + O_2 \longrightarrow 2Li_2O \text{ (Oxide)}$$

$$Na + O_2 \longrightarrow Na_2O_2 \text{ (Peroxide)}$$

$$M + O_2 \longrightarrow MO_2 \text{ (Superoxide)}$$

ii. **Reaction with Water:** The alkali metals on reaction with water form their respective hydroxide and dihydrogen.

$$2M + 2H_2O \longrightarrow 2M^+ + 2OH^- + H_2$$

(M = an alkali metal)

iii. **Reaction with Dihydrogen:** Alkali metal react with dry di-hydrogen at about 673K (lithium at 1073K) to form crystalline hydrides which are ionic in nature and have high melting points.

$$2M + H_2 \longrightarrow 2M^+H^-$$

iv. **Reaction with Halogens:** The alkali metals react vigorously with halogens and form halides which are ionic in nature, M^+X^-. But the halides of lithium are a bit covalent in nature.

v. **Reaction with Mercury:** The alkali metals have strong tendency to get oxidised, that is why they act as strong reducing agents, among this lithium is the strongest and sodium is the least powerful reducing agent.

vi. **Reducing Nature:** Alkali metals combine with mercury to form amalgams. The reaction is highly exothermic in nature.

$$Na + Hg \longrightarrow Na[Hg]$$

vii. **Solutions in liquid Ammonia:** All alkali metals dissolve in liquid ammonia and give deep blue colour solution which are conducting in nature. These solutions contain ammoniated cations and ammoniated electrons as shown below:

$$M + (x + y)NH_3 \longrightarrow [M(NH_3)x]+ + [e(NH_3)y]^-$$

Uses of Alkali Metals

1. Lithium is used as a metal in a number of alloys. Its alloys with aluminium to make aircraft parts.
2. Lithium hydroxides is used in the ventilation systems of space crafts and submarines to absorb carbondioxide.
3. Lithium aluminium hydride ($LiAlH_4$) is a powerful reducing agent which is commonly used in organic synthesis.
4. Liquid sodium or its alloys with potassium is used as a coolant in nuclear reactors.
5. Sodium-lead alloy is used for the preparation of tetraethyl lead, $Pb(C_2H_5)_4$, which is used as an antiknocking agent in petrol.
6. Sodium is used in the production of sodium vapour lamps.
7. Potassium chloride is used as fertilizer.
8. Potassium hydroxide is used in the manufacture of soft soaps and also as absorbent of carbon dioxide.
9. Potassium ions play a vital role in biological systems.
10. Caesium is used in photoelectric cells.

Anomalous Properties of Lithium

Lithium shows properties which are very different from the other members of its group. This is due to the:

1. Exceptionally small size of its atom and ion.
2. Greater polarizing power of lithium ion.
3. As compared to other alkali metals, lithium is harder and its melting point and boiling point are higher.
4. Among all the alkali metals lithium is least reactive but the strongest reducing agent.

Some important Compounds of Sodium

Sodium is highly reactive and always found in combined state. The isotope of sodium (Na) is used in detection of leukemia. The compound of sodium is given below:

1. **Sodium Oxide (Na_2O)**

   Preparation:

   $$2NaNO_2 + 6Na \longrightarrow 4Na_2O + N_2$$

   Properties:

   1. Sodium oxide is a colourless ionic solid.
   2. Aqueous solution of sodium oxide is strongly basic.
   3. Sodium oxide on reaction with liquid ammonia forms sodamide.
   4. At low temperature, when sodium peroxide is reacted with water or acids, H_2O_2 is formed.

2. **Sodium Peroxide (Na_2O_2)**

   Preparation:

   Sodium when heated in excess of air or when heated in excess of pure oxygen gives sodium peroxide.

   $$2Na + O_2 \longrightarrow Na_2O_2$$

   Properties:

   1. Sodium peroxide is a pale yellow diamagnetic compound.
   2. Sodium peroxide is a powerful oxidising agent.
   3. Sodium peroxide combines with CO and CO_2 to give carbonate.
   4. At low temperature, when sodium peroxide is reacted with water or acids, H_2O_2 is formed.

   $$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

3. **Sodium Hydroxide (Caustic Soda) (NaOH)**

Preparation:

When sodium carbonate is treated with calcium hydroxide it give calcium carbonate along with sodium hydroxide. Also known as lime caustic soda process. It is a reversible reaction.

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3$$

Properties

1. Sodium hydroxide is a white crystalline deliquescent solid.
2. Sodium hydroxide is corrosive in nature.
3. Sodium hydroxide is highly soluble in water.
4. Sodium hydroxide reacts with acid forming corresponding salts.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Uses:

It is used in the manufacture of soap, paper, artificial silk and a number of chemicals,

1. In petroleum refining.
2. In the purification of bauxite.
3. In the textile industries for mercerising cotton fabrics.
4. For the preparation of pure fats and oils.
5. As a laboratory reagent.

4. **Sodium Carbonate (Na_2CO_3)**

Preparation:

$$NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$$

$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$$

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

Properties:

1. Sodium carbonate is a white crystalline solid.
2. $Na_2CO_3.10H_2O$ is known as washing soda.
3. Sodium carbonate reacts with acids to give carbon dioxide.

Uses:

1. It is used in water softening, laundering and cleaning.
2. It is used in the manufacture of glass, soap, borax and caustic soda.
3. It is used in paper, paints and textile industries.
4. It is an important laboratory reagent both in qualitative and quantitative analysis.

$$Na_2CO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$

Properties:

On heating sodium bicarbonate loses CO_2 and H_2O forming Na_2CO_3.

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

5. **Sodium Chloride (NaCl)**

Manufacture of sodium chloride is done from sea water. Sea water is allowed to dry up under summer heat in small tanks and solid crust so formed is collected.

Properties:

1. Sodium chloride is a white crystalline solid.
2. It is slightly hygroscopic.
3. It is soluble in water and insoluble in alcohol.

Uses:

1. It is used as a common salt or table salt for domestic purpose.
2. It is used for the preparation of Na_2O_2, NaOH and Na_2CO_3.

6. **Sodium Bicarbonate (Baking Soda) ($NaHCO_3$)**

Preparation:

When NaOH is treated with CO_2 in presence of H_2O it gives sodium bicarbonate.

$$NaOH + CO_2 + H_2O \longrightarrow NaHCO_3$$

Properties:

On heating sodium bicarbonate loses CO_2 and H_2O forming Na_2CO_3.

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

Group-2 Elements: Alkaline Earth Metals

The elements of group-2 are Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra). Except for Be, rest are known as alkaline earth metals, because they were alkaline in nature and existed in the earth.

1. **Electronic Configuration**

The alkaline earth metals have 2 electrons in the s-orbital of the valence shell. Their general electronic configuration [Noble gas]ns^2

Element	Symbol	Electronic configuration
Beryllium	Be	$1s^22s^2$
Magnesium	Mg	$1s^22s^22p^63s^2$
Calcium	Ca	$1s^22s^22p^63s^23p^64s^2$
Strontium	Sr	$1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^2$
Barium	Ba	$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^66s^2$ or $[Xe]\ 6s^2$
Radium	Ra	$[Rn]7s^2$

2. **Atomic and Ionic Radii**

The atomic radii as well as ionic radii of the members of the family are smaller than the corresponding members of alkali metals. Within the group, the atomic and ionic radii increase with increase in atomic number.

3. **Ionization Enthalpies**

The alkaline earth metals owing to their large size of atoms have fairly low values of ionization enthalpies. Within the group, the ionization enthalpy decreases as the atomic number increases.

4. **Hydration Enthalpies**

The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Therefore, compounds of alkaline earth metals are more extensively hydrated, for example, magnesium chloride and calcium chloride exist. the hydration enthalpies of alkaline earth metal ions decrease with increase in ionic size down the group. $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

5. **Physical Properties**

The alkaline earth metals are silvery white, lustrous and relatively soft but harder than the alkali metals. The melting and boiling points of these metals are higher than the corresponding alkali metals. The electropositive character increases down the group from Be to Ba, Calcium, strontium and barium impart characteristic brick red, crimson and apple green colours respectively to the flame. The alkaline earth metals just like those of alkali metals have high electrical and thermal conductivities.

6. **Chemical Properties**

As compared to alkali metals, alkaline earth metals are less reactive due to their relatively higher ionization enthalpies. The reactivity of alkaline earth metals increases on going down the group.

i. **Reaction with water:** Ca Sr, and Ba have reduction potentials similar to those of corresponding group Ist metals and are quite high in the electrochemical series. They react with cold water readily, liberating hydrogen forming metal hydroxides.

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

ii. **Reaction with Air:** Except Be these metals are easily tarnished in air as a layer of oxide is formed on their surface. Ba in powdered form bursts into flame on exposure to air.

iii. **Reaction with hydrogen:** The elements Mg, Ca, Sr and Ba all react with hydrogen to form hydrides MH_2.

iv. **Reaction with oxygen:** Except Ba and Ra the elements when burnt in oxygen form oxides of the type MO.

v. **Reaction with halogens:** When heated with halogens the alkaline earth metals directly combine with them and form the halides of the type MX_2.

$$Ca + Cl_2 \longrightarrow CaCl_2$$

vi. **Reaction with acids:** The alkaline earth metals readily react with acids liberating dihydrogen.

$$M + 2HCl \longrightarrow MCl_2 + H_2$$

Uses of alkaline earth metals:

1. Beryllium is used in the manufacture of alloys. Cooper-Beryllium alloys are used in the making of high strength springs.
2. Metallic beryllium is used for making windows of X-rays tubes.
3. Magnesium, being a light metal, forms many light alloys with aluminum, zinc, manganese and tin.
4. Magnesium is used in flash powders and bulbs, incendiary bombs and signals.
5. Magnesium-aluminium alloys are used in aircraft construction.
6. Magnesium is used as sacrificial anode for the prevention of corrosion of iron.
7. A suspension of magnesium hydroxide in water (called milk of magnesia) is used as an ant-acid to control excess acidity in stomach.
8. Magnesium carbonate is an ingredient of tooth-paste.
9. Calcium is used in the extraction of metals from oxides which are difficult to reduce with carbon.
10. Calcium and barium metals are used to remove air from vacuum tubes, due to their tendency to react with oxygen and nitrogen at high temperature.
11. Radium salts are used for radio therapy of cancer.

Anomalous Behaviour of Beryllium

Beryllium shows different behaviour from the rest members of its group and shows diagonal relationship to aluminium due to reasons discussed below.

1. Beryllium has exceptionally small atomic and ionic sizes and therefore does not compare well with other members of the group, because of high ionisation enthalpy and small size it forms compounds which are largely covalent and get easily hydrolysed.
2. Beryllium does not exhibit coordination number more than four as in its valence shell, there are only four orbitals. The remaining members of the group can have a coordination number of six by making use of d-orbitals.
3. The oxides and hydroxide of beryllium unlike the hydroxide of other elements in the group, are amphoteric in nature.

Compounds of Calcium

1. **Calcium Oxide (CaO)**

Preparation:

Calcium carbonate when decomposed at 800°C gives calcium oxide.

$$CaCO_3 \longrightarrow CaO + CO_2$$

Properties:

1. Calcium oxide is also known as 'Quick lime' or 'Burnt lime', is white amorphous substance.
2. When water is added to lime a hissing sound is produced along with clouds of steam. The lime forms slaked lime [$Ca(OH)_2$].
3. Calcium oxide reacts with moist chlorine to form bleaching powder.

$$CaO + Cl_2 \longrightarrow CaOCl_2$$

4. Calcium oxide on reaction with moist HCl gas forms $CaCl_2$.

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$$

2. **Calcium Carbonate ($CaCO_3$)**

Preparation:

Carbon dioxide when passed through lime water gives calcium carbonate.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

Properties:

1. Calcium carbonate is a white powder insoluble in water.
2. Calcium carbonate dissolves in water in presence of CO_2 due to formation of calcium bicarbonate.

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

3. **Calcium Chloride ($CaCl_2$)**

Preparation:

Calcium oxide, calcium hydroxide or calcium carbonate when treated with HCl gives calcium chloride.

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$$

Properties:

1. Calcium chloride is a colourless deliquescent crystalline substance which is soluble in water as well as in alcohol.
2. Crystals of calcium chloride when strongly heated gives off water of crystallizations.

4. **Calcium sulphate (Plaster of Paris)**

Preparation:

When Gypsum is heated at about 120° - 130°C, Plaster of Paris is formed.

$$2CaSO_4 + 4H_2O \longrightarrow (CaSO_4)2H_2O + 3H_2O$$

Properties:

1. It is a white crystalline solid. It is sparingly soluble in water.
2. It becomes anhydrous at about 200°C. Anhydrous form is known as dead burnt plaster.

5. **Calcium hydroxide $Ca(OH)_2$**

Preparation:

$$CaO + H_2O \longrightarrow Ca(OH)2$$

Properties:

1. It gives $CaCO_3$ and $Ca(HCO_3)_2$ with CO_2

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

2. On prolong treatment with CO_2 milkiness disappears due to formation of $Ca(HCO_3)_2$

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO3)_2$$

Diagonal Relationship of Lithium with Magnesium

The main points of similarity:

(1) Both have almost similar electronegativities.

(2) Both Li and Mg are quite hard. They are harder and lighter than other elements in their respective groups.

(3) Both LiOH and $Mg(OH)_2$ are weak bases.

(4) Both form ionic nitrides when heated in atmosphere of Nitrogen.

$$6\ Li + N_2 \rightarrow 2\ Li_3N$$

$$3\ Mg + N_2 \rightarrow 2\ Mg_3N_2$$

(5) The hydroxides of both lithium and magnesium decompose upon heating.

$$2\ LiOH \rightarrow Li_2O + H_2O$$

$$Mg\ (OH)_2 \rightarrow MgO + H_2O$$

(6) Both lithium and magnesium combine with oxygen to form monooxide while other members of their respective groups form peroxide and superoxide.

$$4\ Li + O_2 \rightarrow 2\ Li_2O$$

$$2\ Mg + O_2 \rightarrow 2\ MgO$$

The Li_2O and MgO thus formed do not combine with excess O_2 to form peroxide and superoxide.

(7) The carbonates of these metals decompose on heating to the corresponding oxides with the evolution of carbon dioxide.

$$Li_2CO_3 \rightarrow Li_2O + CO_2$$

$$MgCO_3 \rightarrow MgO + CO_2$$

(8) Both Lithium and magnesium do not form solid bicarbonates.

(9) Both Lithium and magnesium nitrate decompose on heating producing nitrogen dioxide.

$$4\ LiNO_3 \rightarrow 2\ Li_2O + 4\ NO_2 + O_2$$

$$2\ Mg\ (NO_3)\ 2 \rightarrow MgO + 4\ NO_2 + O_2$$

(10) The hydroxides, carbonate, oxalates, phosphates and fluorides of both Lithium and magnesium are sparingly soluble in water.

(11) Because of the covalent character, LiCl and $MgCl_2$ are soluble in ethanol.

(12) Both Lithium perchlorate and magnesium perchlorate are highly soluble in ethanol.

(13) LiCl and $MgCl_2$ are deliquescent and crystallise from aqueous solution as hydrate $LiCl\cdot 2\ H_2O$ and $MgCl_2\cdot 6\ H_2O$.

Extraction of Alkali Metals

Alkali metals cannot be extracted from their ores by the usual methods of extraction of metals because of following difficulties:

1) Alkali metals are strong reducing agents and hence cannot be extracted by reduction of their oxides or chlorides.

2) Alkali metals being highly electropositive cannot be displaced from the aqueous solution of their salts by other metals.

3) Alkali metals cannot be isolated by electrolysis of the aqueous solution of their salts since hydrogen is liberated at the cathode instead of the alkali metal because the standard electrode potentials of alkali metals are much lower than that of water. By using mercury as cathode, the alkali metals can be deposited at the cathode but the alkali metals so deposited readily combines with mercury to form an amalgam from which its recovery is very difficult.

Extraction of Lithium

Lithium is prepared by electrolysis of fused mixture of dry lithium chloride and potassium chloride at 723 k.

Potassium chloride is added to increase the conductivity of lithium chloride and also to lower the fusion temperature. The cell is operated at a temperature of about 723 K and current voltage of 8-9 V.

As a result of electrolysis, the following reactions takes place:

$$LiCl \Leftrightarrow Li^+ + Cl^-$$

At cathode: $Li^+ + e^- \longrightarrow Li$

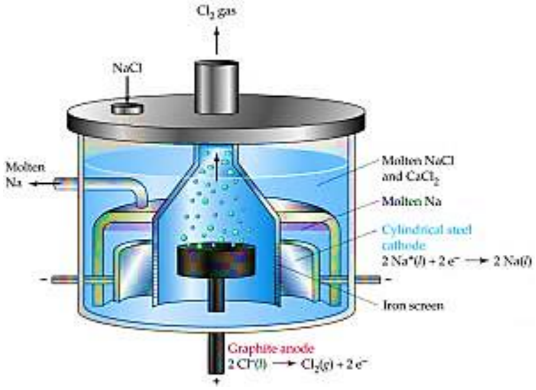
At anode: $2\,Cl^- - 2e^- \longrightarrow Cl_2$

The metal thus obtained is 99% pure and is stored by keeping it wrapped in paraffin wax. Lithium being the lightest metal known cannot be stored in kerosene oil since it floats on the surface.

Uses of Lithium

1) It is used in the manufacture of alloys
    a) Lithium – lead alloy or white metal which is used for making toughened bearing for motor engines and sheats for cables.
    b) Lithium aluminium alloy has great tensile strength and electricity like that of mild steel. It is used for aircraft construction.
    c) Lithium magnesium alloy is extremely tough and corrosion resistant which is used for armour plate and aerospace components.
2) It is used for producing thermonuclear energy required for propelling rockets and guided missiles.
3) Lithium is used to make both primary and secondary batteries.
4) Lithium is used as a Scavenger since it combines readily with oxygen and nitrogen. Thus, it is used for removing little traces of oxygen and nitrogen during refining of metals.
5) lithium carbonate is used in making a special variety of glass which is very strong and is weather proof.
6) Lithium chloride is used in Air conditioning plants to regulate the humidity. It is also used in Ni-Fe accumulators.
7) Lithium Bromide is used in medicine as sedative.
8) Lithium bicarbonate and lithium salicylate have been used for treatment of rheumatism since the resulting Lithium urinate is soluble in water.
9) Lithium hydride is used as source of hydrogen for meterological purpose and for filling of balloons.
10) Lithium Hydroxide is used for removing carbon dioxide from exhaled air in closed quarters.
11) Lithium aluminium hydride is used as a reducing agent in synthetic organic chemistry.

Extraction of Sodium



Sodium is extracted by the electrolysis of fused sodium chloride by a process called Down's process.

Sodium is now obtained by electrolysis of a fused eutectic mixture of sodium chloride and calcium chloride in Down's cell at 873 K using graphite anode and iron cathodes.

As a result of electrolysis, sodium is liberated at the cathode and Cl_2 is evolved at the anode.

$$NaCl \longrightarrow Na^+ + Cl^-$$

At cathode: $Na^+ + e^- \longrightarrow Na$

At anode: $Cl^- \longrightarrow Cl + e^-$

$$Cl + Cl \longrightarrow Cl^2$$

Uses of Sodium

1) Sodium is used as a reducing agent in the extraction of boron and silicon.
2) Sodium is employed as a reducing agent in form of sodium amalgam and as a reagent in Wurtz reaction and in the synthesis of many organic compound.
3) It is also used to make tetraethyl lead, tetra methyl lead which are used as anti-knocking agent for gasoline.
4) liquid Na or its alloys with potassium is used as a coolant in fast breeder nuclear reactor.
5) It is used in the manufacture of number of chemicals such as Na_2O_2, NaCN, $NaNH_2$.
6) It is used in sodium vapour lamp.
7) Sodium is largely used in industry for the production of artificial rubber , dyes, drugs.
8) Because of its lightness and high thermal conductivity, it is used for filling exhaust valves of aeroplane engines.

Use of Potassium

1) It has a vital role in biological system.
2) KCl is used as fertilizer.
3) KOH is used in manufacture of soap.
4) It is also used as an excellent absorbent for Carbon dioxide.

Baking Soda and Sodium Chloride

Sodium chloride (NaCl)

The most abundant source of sodium chloride is sea water which contains 2.7 - 2.9% by mass.

Common salt is generally obtained by evaporation of sea water. Crude sodium chloride obtained by crystallisation of brine solution contains impurities of sodium sulphate (Na_2SO_4), calcium sulphate ($CaSO_4$), calcium chloride ($CaCl_2$) magnesium chloride ($MgCl_2$).

Since $MgCl_2$ and $CaCl_2$ are deliquescent (absorb moisture easily from the atmosphere), therefore, impure common salt gets wet in rainy season. To obtain pure sodium chloride, the crude salt is dissolved in minimum amount of water and filtered to remove insoluble impurities. The solution is then saturated with HCl gas when crystals of pure sodium chloride separate out. The solution is then saturated with hydrogen chloride gas when crystals of pure sodium chloride separate out. The calcium and magnesium chloride being more soluble remains in the solution.

Properties

1) Sodium chloride melts at 1081 K.

2) Its solubility is 3.6 g per 100 g of H_2O at 273 K. The solubility does not increase appreciably with rise in temperature.

Uses

1) It is used as a common salt for domestic purpose.
2) It is used in the preparation of Na_2CO_3, NaOH, Na_2O_2.

Baking soda or Sodium hydrogen carbonate ($NaHCO_3$)

Sodium hydrogen carbonate is commonly called baking soda because on heating it decomposes to evolve bubbles of carbon dioxide.

Preparation

It is prepared by saturating a solution of sodium carbonate with carbon dioxide. Being less soluble, white crystalline powder of sodium hydrogen carbonate gets separated.

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2\ NaHCO_3$$

Uses

1) It is used in fire extinguishers for generating CO_2.

$$NaHCO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O$$

2) It is used in the preparation of baking powder which is a mixture of $NaHCO_3$, starch, calcium dihydrogen phosphate $Ca(H_2PO_4)$, sodium Aluminium Sulphate $NaAl\ (SO_4)_2$.
3) It is a mild antiseptic for skin infections.
4) It is used as an antacid in making digestive powders for removing acidity of stomach.

Cement

Cement is essentially a finely powdered mixture of calcium silicate and aluminates along with small quantities of gypsum which sets into a hard stone like mass when treated with water.

Average composition of Portland cement

Cement is obtained by combining a material rich in lime, CaO with other materials such as clay, which contains silica, SiO2 along with oxides of aluminium, iron and magnesium.

Lime (CaO) 50 - 60%

Magnesium oxide (MgO) 2 - 3%

Silica (SiO_2) 20 - 25%

Ferric oxide (Fe_2O_3) 1 - 2%

Alumina (Al_2O_3) 5 - 10%

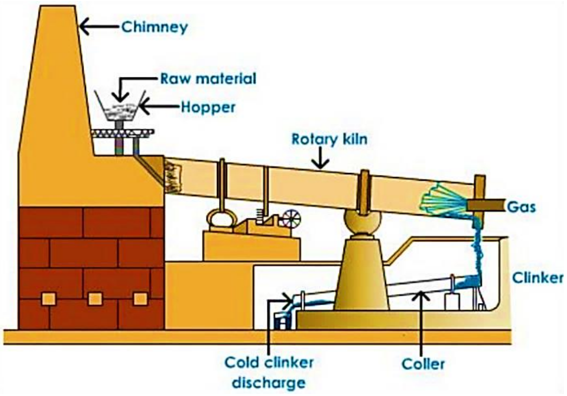
Sulphur trioxide (SO_3) 1 - 2%

For a good quality cement, the ratio of alumina to silica should lie between 2.5 to 4 while that of lime to that of silica, alumina and ferric oxide should be as close to 2 as possible.

Raw material

Raw materials required for the manufacture of cement are 1) limestone ($CaCO_3$) ,2) clay which provides both silica and Alumina 3) gypsum. Small amount of magnesia and iron oxide are also required for imparting suitable colour to cement.

Manufacture of cement



Cement is manufactured by two processes:

(1) Wet process

(2) Dry process

The wet process is preferred when the raw materials i.e., limestone and clay are soft, climate is humid and fuel is cheap. The dry process is preferred when the raw materials are hard.

The main raw materials are limestone and clay. Wet process supplies lime while the dry process is a source of silica, alumina and iron oxides.

(1) The raw materials are first crushed separately in a suitable machine. They are then mixed in the required proportion (3 parts limestone + 1 part clay) and grounded together finely. This grinding is done either by the dry process or by the wet process.

(2) In the wet process, the clay is washed with water in a wash mill to remove flint and other foreign substances. It is then mixed with requisite quantity of limestone and pulverised in a special mill. The resulting pasty mass is then throughly homogenised to get raw slurry containing about 40% water.

(3) In the dry process, the raw materials are dried and mixed in desired proportion. The mixture is then finely powdered and passed through 300 mesh sieves and homogenised with the help of compressed air. The homogeneous mass is called raw meal.

(4) The slurry or raw meal is introduced into the upper end of a rotary kiln by means of screw conveyer. The kiln consist of an inclined steel rotating cylinder, 150-200 ft long and about 10 ft diameter lined inside with fire bricks. The charge travel downwards slowly due to the rotatory motion given to the kiln and is heated by burning coal dust which is blown in front from the lower end. The charge takes about 2-3 hours to cover the entire journey in the kiln.

The following changes occur:

(1) In the upper part of the kiln, the temperature is around 1000-1100K. Here the charge loses all its water due to evaporation by hot gases.

(2) In the middle of the kiln, temperature is around 1100-1200 K. Here limestone decomposes to form calcium oxide and carbon dioxide.

$$CaCO_{W} \longrightarrow CaO + CO_2$$

(3) The lower part of the kiln, from where coal dust is blown in is the hottest with the temperature ranging between 1770-1870 K. As the charge reaches here, chemical combination takes place between lime, alumina and silica to form calcium silicate and aluminates.

$$2\ CaO + SiO_2 \longrightarrow 2\ CaO.SiO_2$$

$$3\ CaO + SiO_2 \longrightarrow 3\ CaO.SiO_2$$

$$3\ CaO + Al2O_3 \longrightarrow 3\ CaO.Al_2O_3$$

$$2\ CaO + Al2O_3 \longrightarrow 2\ CaO.Al_2O_3$$

$$4\ CaO + Al_2O_3 + Fe_2O_3 \longrightarrow 4\ CaO.\ Al_2O_3.Fe_2O_3$$

Due to very high temperature in this zone, about 20-30 % combines with solid mass to form grey-colored balls called cements clinkers.

The hot clinkers are cooled by cold air and are mixed with 2-3 % gypsum and finely powdered to 325 mesh size in grinding machine. The fine powder called the Portland cement is sieved and packed in bags.

Setting of cement

The important constituents present in Portland cement are dicalcium silicate (Ca_2SiO_4), tricalcium silicate (Ca_3SiO_5) and tricalcium aluminate ($Ca_3Al_2O_6$).

When water is added to cement, an exothermic reaction occurs. During this process, cement reacts with water to form a gelatinous mass which slowly sets into a hard mass having three-dimensional network structure involving -Si-O-Si- and -Si-O-Al chains.

Tricalcium silicate sets quickly and develops considerable strength within a few days. Dicalcium silicate sets slowly and develops appreciable strength after a month or so. Tricalcium aluminate sets instantaneously in presence of water. The internal strength acquired by cement is primarily due to the setting of tricalcium aluminate.

Summary-

1. **s-block elements:** The elements in which last electron enters into s-orbital are called s-block elements.
2. **Alkali metals:** The elements of group 1 whose hydroxide are strong alkali.
3. **Alkaline earth metal:** The elements of group 2, and their oxides and hydroxides are alkaline in nature and their oxides are found in the Earth's crust.
4. **Diagonal relationship:** The resemblance in properties of elements of second period with elements of third period present diagonally on the right-hand side.
5. Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.

Class : 11th Chemistry
Chapter- 10: S- Block Elements

S- Block Elements

Group 2 Elements (Alkaline Earth Metals)

- Atomic and Ionic Radii: Smaller than corresponding alkali ir group,increases with increase in atomic number.
- I.E:IE$_1$ higher than corresponding Group 1 metals.
  IE$_2$ smaller than corresponding alkali metals.
- Hydration Enthalpies: Decreases with increase in ionic size down the group.

Physical properties:

- Slivery white, lustrous and relatively soft but harder than alkali metals.
- M.p. and b.p. higher than corresponding alkali metals.
- Electropositive character increases down the group.

Chemical properties:

- Be and Mg are kinetically inert to O and H_2O
- Mg is more electropositive and burns in air.
- Ca, Sr and Ba with air forms oxide and nitride.

$M + X_2 \longrightarrow MX_2 (X = F, Cl, Br, I)$

$2BeCl_2 + LiAlH_4 \longrightarrow 2BeH_2 + LiCl + AlCl_3$

$M + 2HCl \longrightarrow MCl_2 + H_2$

$M + (x+y)NH_3 \longrightarrow [M(NH_3)_x]^{2+} + 2[e(NH_3)_y]^-$

Uses:

- Be is used in the manufacture of alloys.
- Metallic Be is used for making windows of X–rays tubes.
- Mg-Al alloys are used in air craft construction.
- Ca in extraction of metals.
- Ra is used in radiotherapy.

Characteristics of Compounds of Alkaline Earth Metals:

- **Oxides and Hydroxides**
- Alkaline earth metals burn oxygen to form MO.
- All oxides except BeO are basic in nature

$MO + H_2O \longrightarrow M(OH)_2$

$Be(OH)_2$ is amphoteric in nature

Halides:

- Except for Be halides, all other halides are ionic.
- Tendency to form halide hydrates decreases gradually.
- Salts of oxoacids: Forms carbonates, sulphates and nitrates.
- Anomalous behavior of Be: Small atomic and ionic sizes, does not exhibit C.N. more than four, its oxide and hydroxide are amphoteric.
- Be shows diagonal relationship with Al.

Biological Importance Of Mg And Ca:

- All enzymes that utilise ATP in PO_4 transfer requires Mg as cofactor. Chlorophyll contains Mg. Ca is present in bones and teeth. Important in neuromuscular function, intraneuronal transmission and blood coagulation.

Group 1 Elements (Alkali Metals)

- **Atomic and Ionic Radii:** Increases with increase in atomic number.
- **I.E.:** Decreases down the group.
- **Hydration Enthalpy:** Decreases with increase in ionic sizes.
- **Physical properties:**
- Silvery white, soft and light metals.
- Low m.p. and b.p.
- Alkali metals and their salts impart colour to an oxidizing flame.

Chemical Properties:

$4Li + O_2 \rightarrow 2Li_2O$; $2Na + O_2 \rightarrow Na_2O_2$; $M + O_2 \rightarrow MO_2$ (M=K, Rb, Cs)

$2M + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2$

$2M + H_2 \rightarrow 2M^+H^-$

React vigorously with halogens to form ionic halides

$M + (x+y) NH_3 \rightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$

Uses:

- Li is used to make useful alloys.
- Li is used in thermonuclear reactions and making electrochemical cells.
- Na is used to make Na/Pb alloy.
- Liquid Na metal is used as coolant in nuclear reactors.
- KCl is used as fertilizer.
- Cs is used in devising photoelectric cells.

Characteristics Of Compounds Of Alkali Metals:

– Oxide and Hydroxides

$$\text{Combustion in excess of air} \begin{cases} \xrightarrow{+Li} Li_2O \\ \xrightarrow{+Na} Na_2O_2 \\ \xrightarrow{+K/Rb/Cs} MO_2 \end{cases}$$

- Halides
  - Alkali metal halides (MX) have high melting, colourless crystalline solids.
  - Preparation: Reaction of oxide, hydroxide or carbonate with aq HX.
  - High negative enthalpies of formation.
  - Melting and boiling points: F >Cl> Br > I
  - Soluble in water.

Salts of Oxo-Acids:

- Alkali metals form salts with all oxo-acids.
- Soluble in water and thermally stable.
- Stability of carbonates and hydrogencarbonates increases

Anomalies properties of Li: Due to

(i) exceptionally small size of its atom and ion.

(ii) High polarising power.

Biological Importance of Na and K:

Na ions participate in nuclear signals transmission, regulator of flow of water across cell membranes. K ions activate many enzymes and oxidation of glucose to produce ATP.

Important Compounds of Calcium

(i) CaO, Quick Lime

Preparations: $CaCO_3 \overset{heat}{\rightleftharpoons} CaO + CO_2$

Properties : White amorphous solid with m.p. 2870 K

$CaO + H_2O \longrightarrow Ca(OH)_2$, $CaO + CO_2 \longrightarrow CaCO_3$

(ii)$Ca(OH)_2$ Calcium hydroxide : Preparations: Additional of water to CaO.

Properties: white amorphous powder .

$Ca(OH_2) + CO_2 \longrightarrow CaCO_3 + H_2O$

(iii)$CaSO_4$. ½H_2O(Plaster of Paris)

$2(CaSO_4.2H_2O) \longrightarrow 2(CaSO_4).H_2O + 3H_2O$

Electronic Configuration

ns^1 : Alkaline metals; ns^2 : Alkaline earth metals

Important Compounds of Sodium:

(i)Sodium Carbonate (Washing Soda): Preparation: By Solvay process $2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2 CO_3$

$(NH_4)_2CO_3 + H_2O + CO_2 \rightarrow 2NH_4HCO_3$

$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$

$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + H_2O$

Properties: (a)White, crystalline solid. (b)Readily soluble in water

$Na_2CO_3 \cdot 10H_2O \xrightarrow{375K} Na_2CO_3 \times H_2O + 9H_2O$

$Na_2CO_3 \cdot H_2O \xrightarrow{>373K} Na_2CO_3 + H_2O$

Uses: Water softening, laundering, cleaning, manufacture, as laboratory reagent.

(*i*)Sodium Chloride *(Nacl)*

Preparation: Crude NaCl by crystallization of brine solution.

-Pure NaCl is obtained by dissolving crude salt in minimum water and filtered to remove insoluble impurities. Solution is saturated with HCl gas. Uses: As common salt.

(ii)Sodium Hydroxide (NaOH)

Preparation: By electrolysis of NaCl in Castner-Kellner cel.

Uses: In manufacture of soap, paper, petroleum refining.

(iii)Sodium Hydrogencarbonate ($NaHCO_3$)

Preparation: $Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$

Important Questions

Multiple Choice questions-

1. Beryllium shows diagonal relationship with
   (a) Mg
   (b) Na
   (c) Al
   (d) B.
2. Which of the following metal has stable carbonates?
   (a) Na
   (b) Mg
   (c) Al
   (d) Si
3. The reaction of Cl_2 with X gives bleaching powder X is
   (a) CaO
   (b) $Ca(OH)_2$
   (c) $Ca(OCl)_2$
   (d) $Ca(O_3Cl)_2$
4. NaOH is prepared by the method
   (a) Downs cell
   (b) Castner cell
   (c) Solvay process
   (d) Castner – Kellner cell.
5. Milk of lime reacts with chlorine to form _______, a constituent of bleaching powder.
   (a) $Ca(OCI)_2$
   (b) $Ca(CIO_2)_2$
   (c) $Ca(CIO_3)_2$
   (d) $Ca(CIO_4)_2$
6. Which one of these are main components of kidney stones?
   (a) Sodium Oxalate
   (b) Potassium Oxalate
   (c) Calcium Oxalate
   (d) Copper Oxalate
7. A nitrate of an alkali metal M on heating gives $O_2.NO_2$ and M_2O. The metal M will be:
   (a) Na
   (b) K
   (c) Rb
   (d) Li
8. Which of the following metal carbonates decompose on heating?
   (a) $LiCO_3$ & $MgCO_3$
   (b) Na_2CO_3
   (c) K_2CO_3
   (d) None of the Above
9. Which of the following alkaline earth metals do not impart any color to the flame?
   (a) Ca,Sr
   (b) Mg,Ca
   (c) Be,Mg
   (d) Sr,Ba
10. Which one of the following alkali metals emit light of longest wavelength in the flame test?
    (a) Na
    (b) K
    (c) Cs
    (d) Li
11. What will be final weight of 286 gm $Na_2CO_3.10H_2O$ by Heating at 373 K?
    (a) 206 gm
    (b) 162 gm
    (c) 186 gm
    (d) 124 gm
12. Solubilities of carbonates decrease down the magnesium group due to decrease in
    (a) Entropy of solution formation
    (b) Lattice energies of solids
    (c) Hydration energy of cations
    (d) Inter – ionic attraction.
13. What are the products formed when Li_2CO_3 undergoes decomposition?
    (a) Li_2O_2, CO
    (b) Li_2O, CO
    (c) Li_2O, CO_2
    (d) LiO_2, CO
14. Alkali metals give a _______ when dissolved in liquid ammonia
    (a) Deep blue solution
    (b) Colorless
    (c) Red colour
    (d) None of the Above

15. ______ does not exhibit coordination number more than four.
    (a) Magnesium
    (b) Beryllium
    (c) Calcium
    (d) None of the Above

Very Short:

1. Which element is found in chlorophyll?
2. Name the elements (alkali metals) which form superoxide when heated in excess of air.
3. Why is the oxidation state of Na and K always + 1?
4. Name the metal which floats on the water without any apparent reaction with water.
5. Why do group 1 elements have the lowest ionisation enthalpy?
6. Why does the following reaction
7. Amongst Li, Na, K, Rb, Cs, Fr which one has the highest and which one has the lowest ionisation enthalpy?
8. What is the general electronic configuration of alkali metals in their outermost shells?
9. What is meant by dead burnt plaster?
10. Name three forms of calcium carbonate.

Short Questions:

1. Why the solubility of alkaline metal hydroxides increases down the group?
2. Why the solubility of alkaline earth metal carbonates and sulphates decreases down the group?
3. Why cannot potassium carbonate be prepared by the SOLVAY process?
4. What are the main uses of calcium and magnesium?
5. What is meant by the diagonal relationship in the periodic table? What is it due to?
6. Why is the density of potassium less than that of sodium?

Long Questions:

1. Why is it that the s-block elements never occur in a free state? What are their usual modes of occurrence?
2. Explain what happens when:
    (a) Sodium hydrogen carbonate is heated.
    (b) Sodium with Mercury reacts with water.
3. What is the effect of heat on the following compounds?
    (a) Calcium carbonate
    (b) Magnesium chloride hexahydrate
    (c) Gypsum
4. State as to why
    (a) An aqueous solution of sodium carbonate gives an alkaline test.
    (b) Sodium is prepared by electrolytic method & not by chemical method.
    (c) Lithium on being heated in the air mainly forms mono-oxide & not the peroxides.
5. What raw materials are used for making cement? Describe the manufacture of Portland cement. What is its approximate composition?

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): The carbonate of lithium decomposes easily on heating to form lithium oxide and CO_2.

   Reason (R): Lithium being very small in size polarises large carbonate ion leading to the formation of more stable Li_2O and CO_2.

   (i) Both A and R are correct and R is the correct explanation of A.
   (ii) Both A and R are correct but R is not the correct explanation of A.
   (iii) Both A and R are not correct
   (iv) A is not correct but R is correct.

2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): Beryllium carbonate is kept in the atmosphere of carbon dioxide.

   Reason (R): Beryllium carbonate is unstable and decomposes to give beryllium oxide and carbon dioxide.

   (i) Both A and R are correct and R is the correct explanation of A.
   (ii) Both A and R are correct but R is not the correct explanation of A.
   (iii) Both A and R are not correct.
   (iv) A is not correct but R is correct.

Case Study Based Question:

1. Alkali metals have the lowest ionization energy in their corresponding period in periodic table because they have large size which results in a large distance between the nucleus and the outermost electron. Ionization energy of alkali metals decreases from Li to Cs due to increase in atomic size. First ionization energy of alkali metals is very low but they have very high value of second ionization energy.

$$\underset{[noble\ gas]ns^1}{M_{(g)}} \xrightarrow{1^{st}\ I.E.} \underset{[noble\ gas]}{M^+} + e^-$$

Metal	Ionization Energy (kJ mol^{-1})	
	IE$_1$	IE$_2$
Li	520.1	7296
Na	495.7	4563
K	418.6	3051
Rb	402.9	2633
Cs	375.6	2230

(1) Alkali metals are characterised by:
   (a) Good conductors of heat and electricity
   (b) High melting points
   (c) Low oxidation potentials
   (d) High ionisaiton potentials.

(2) Metals dissolve in liquid ammonia giving coloured solutions which are conducting in nature. The colour of the solution and reason of its conductance is:
   (a) Yellow, NH_4^+
   (b) Blue, ammoniated metals
   (c) Orange, $[M(NH_3)_x]^+$
   (d) Blue, ammoniated electron

(3) Alkali metals displace hydrogen from water forming bases due to the reason that:
   (a) They are far above the hydrogen in electrochemical series based on oxidation potential.
   (b) They are far below the hydrogen in electrochemical series based on oxidation potential.
   (c) Their ionization potential is less than that of other elements.
   (d) They contain only one electron in their outermost shell.

2. All alkali metals dissolve and form blue solution in liquid ammonia. When alkali metals are dissolved in liquid ammonia, there is a considerable expansion in total volume hence such solutions are called expanded metals. The blue solution of an alkali metal in ammonia shows certain characteristic properties which are explained on the basis of formation of ammoniated (solvated) metal cations and ammoniated electrons in the metal ammonia solution in the following way:

$$M \longrightarrow M^+ + e^-$$

$$M^+ + xNH_3 \longrightarrow \left[M(NH_3)_x\right]^+$$

$$e^- + yNH_3 \longrightarrow \left[e(NH_3)_y\right]^-$$

Thus,

$$M + (x+y)NH_3 \rightarrow \underset{\text{Ammoniated metal cation}}{\left[M(NH_3)_x\right]^+} + \underset{\text{Ammoniated electron}}{\left[e(NH_3)_y\right]^-}$$

The blue solution is paramagnetic and has high electrical conductivity due to the presence of unpaired electron in the cavities in ammoniacal solution.

(1) Sodium dissolves in liquid NH_3 to give a deep blue solution. This is due to:
   (a) Ammoniated Na^+
   (b) Ammoniated Na^-
   (c) Formation of Na^+/Na^- pair
   (d) Ammoniated electrons.

(2) The increasing order of the density of alkali metals is:
   (a) Li < K < Na < Rb < Cs
   (b) Li < Na < K < Rb < Cs
   (c) Cs < Rb < Na < K < Li
   (d) Cs < Rb < K < Na < Li

(3) The reaction between sodium and water can be made less vigorous by:
   (a) Lowering the temperature
   (b) Adding a little alcohol
   (c) Amalgamating sodium
   (d) Adding a little acetic acid.

Answer Key

MCQ

1. (c) Al
2. (a) Na
3. (c) $Ca(OCl)_2$
4. (d) Castner – Kellner cell.
5. (a) $Ca(OCI)_2$
6. (c) Calcium Oxalate
7. (d) Li
8. (a) $LiCO_3$ & $MgCO_3$
9. (b) Mg, Ca
10. (b) K
11. (d) 124 gm
12. (c) Hydration energy of cations
13. (c) Li_2O, CO_2
14. (a) Deep blue solution
15. (b) Beryllium

Very Short Answer:

1. Magnesium
2. Potassium, rubidium and caesium.
3. It is due to their high second ionisation enthalpy and stability of their ions [Na+, K+].
4. Lithium floats on the water without any apparent reaction to it.
5. Because of the largest size in their respective periods, solitary electron present in the valence shell can be removed by supplying a small amount of energy.
6. Because larger K+ cation stabilizes larger anion.
7. Li has the highest and Fr has the lowest ionisation enthalpy.
8. ns1 where n = 2 to 7.
9. It is anhydrous calcium sulphate ($CaSO_4$).
10. Limestone, chalk, marble.

Short Answer:

1. **Ans:** If the anion and the cation are of comparable size, the cationic radius 'Vill influence the lattice energy. Since lattice energy decreases much more than the hydration energy with increasing ionic size, solubility will increase as we go down the group. This is the case of alkaline earth metal hydroxides.

2. **Ans:** If the anion is large compared to the cation, the lattice; energy will remain almost constant within a particular group. Since the hydration energies decrease down the group, solubility will decrease as found for alkaline earth metal carbonates and sulphates.

3. **Ans:** If the anion is large compared to the cation, the lattice; energy will remain almost constant within a particular group. Since the hydration energies decrease down the group, solubility will decrease as found for alkaline earth metal carbonates and sulphates.

4. **Ans:** Main uses of calcium:
    1. Calcium is used in the extraction of metals from oxides which are difficult to reduce with carbon.
    2. Calcium, due to its affinity for O_2 and N_2 at elevated temperatures, has often been used to remove air from vacuum tubes.

    Main uses of Magnesium:
    1. Magnesium forms alloys with Al, Zn, Mn and Sn. Mg-Al alloys being light in mass are used in aircraft construction.
    2. Magnesium (powder and ribbon) is used in flashbulbs, powders incendiary bombs and signals.
    3. A suspension of $Mg(OH)_2$ in water is used as an antacid in medicine.
    4. Magnesium carbonate is an ingredient of toothpaste.

5. **Ans:** It has been observed that some elements of the second period show similarities with the elements of the third period situated diagonally to each other, though belonging to different groups. This is called a diagonal relationship.

	Group I	Group II	Group III	Group IV
Second period:	Li	Be	B	C
Third period:	Na	Mg	Al	Si

The cause of the diagonal relationship is due to the similarities in properties such as electronegativity, ionisation energy, size etc. between the diagonal elements. For example, on moving from left to right across a period, the electronegativity increases, which on moving down a group, electronegativity decreases. Therefore, on moving diagonally, two opposing tendencies almost cancel out and the electronegativity values remain almost the same as we move diagonally.

6. **Ans:** Generally, in a group density increases with the atomic number, but potassium is an exception. It is due to the reason that the atomic volume of K is nearly twice Na, but its mass (39) is not exactly double of Na (23). Thus, the density of potassium is less than that of sodium.

Long Answer:

1. **Ans:** The elements belonging to s-block in the periodic table. These metals (Alkali & alkaline earth metals) are highly reactive because of their low ionization energy. They are highly electropositive forming positive ions. So, they are never found in a free state. They are widely distributed in nature in a combined state. They occur in the earth's crust in the form of oxides, chlorides, silicates & carbonates.

2. **Ans:** Sodium hydrogen carbonate on heating decomposes to sodium carbonate.

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

When sodium with mercury reacts with water. It produces sodium hydroxide.

$$2Na\,Hg + 2H_2O \xrightarrow{\Delta} 2NaOH + H_2\uparrow + 2Hg$$

3. **Ans:**

$$CaCO_3 \xrightarrow{1070K} CaO + CO_2$$

$$MgCl_2.6H_2O \xrightarrow{\Delta} Mg(OH)Cl + HCl + 5H_2O$$

$$CaSO_4.2H_2O \xrightarrow{120°C} (CaSO_4)_2\,.\,H_2O$$

4. **Ans:** Sodium carbonate gets hydrolise by water to form an alkaline solution.

$$CO3^{2-} + H_2O \rightarrow HCO_3^{-} + OH$$

Due to this, it gives an alkaline test.

Sodium is a very strong reducing agent. Therefore, it cannot be isolated by a general reduction of its oxides or other compounds. The metal formed by electrolysis will immediately react with water forming hydroxides. So, sodium is prepared by the electrolytic method only.

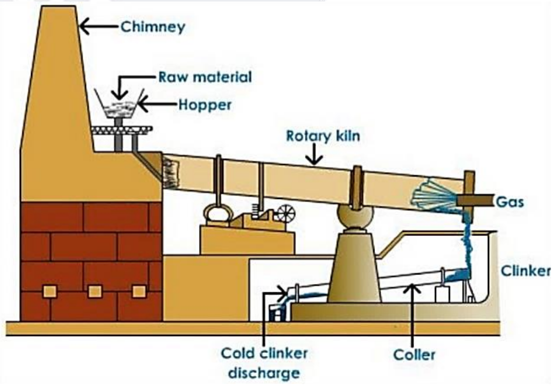
Lithium is the least reactive but the strongest reducing agent of all the alkali metals. It combines with air, it forms mono-oxide only because it does not react with excess air.

$$2Li + \frac{1}{2}O_2 \longrightarrow \underset{(Lithium\ monoxide)}{Li_2O}$$

5. **Ans: Raw materials:** The raw materials required for the manufacture of cement are limestone, stone and clay, limestone in calcium carbonate, $CaCO_3$ and it provides calcium oxide, CaO. Clay- is a hydrated aluminum silicate, Al_2O_3 2Si02.2H20 and it provides alumina as well as silica. A small amount of gypsum, CaS04.2H20 is also required. It is added in calculated quantity in order to adjust the rate of setting of cement.

Manufacture: Cement is made by strongly heating a mixture of limestone and clay in a rotatory kiln. Limestone and clay are finely powdered, and a little water is added to get a thick paste called slurry. The slurry is led into a rotatory kiln from the top through the hopper.

The hot gases produce a temperature of about 1770-1870 K in the kiln. At this high temperature, the limestone and clay present in the slurry combine to form cement in the form of small pieces called clinker. This clinker is mixed with 2 – 3 % by weight of gypsum ($CaSO_4$.$2H_2O$) to regulate the setting time and is then ground to an exceedingly fine powder.



Manufacture of cement

$$Lime\ stone + Clay \xrightarrow{1770\text{–}1870K} \underset{(clinker)}{Cement} + CO_2\uparrow + H_2O\uparrow$$

When mixed with water the cement reacts to form a gelatinous mass which sets to a hard mass when three-dimensional cross-links are formed between

…………..Si — O — Si……… and …….. Si — O — Al…… chains.

Composition of cement:

$CaO = 50 - 60\%$

$SiO_2 = 20 - 25\%$

$Al_2O_3 = 5 - 10\%$

$MgO = 2 - 3\%$

$Fe_2O_3 = 1 - 2\%$

$SO_3 = 1 - 2\%$

For a good quality cement, the ratio of silica (SiO_2) and alumina (Al_2O_3) should be between 2.5 to 4.0. Similarly, the ratio of lime (CaO) to the total oxide mixtures consisting of SiO_2, Al_2O_3 and Fe_2O_3 should be roughly 2: 1. If lime is in excess, the cement cracks during setting. On the other hand, if lime is less than required, the cement is weak in strength. Therefore, the proper composition of cement must be maintained to get cement of good quality.

Assertion Reason Answer:

1. (i) Both A and R are correct and R is the correct explanation of A.
2. (i) Both A and R are correct and R is the correct explanation of A.

Case Study Answer:

1. **Answer:**
   (1) (a) Good conductors of heat and electricity
   (2) (d) Blue, ammoniated electron
   (3) (b) They are far below the hydrogen in electrochemical series based on oxidation potential.
2. **Answer:**
   (1) (d) Ammoniated electrons
   (2) (a) Li < K < Na < Rb < Cs
   (3) (c) Amalgamating sodium.

❖ ❖

The P-Block Elements 11

Introduction

The elements in which last electron enters into p-subshell are called as p-block elements. The number of p-orbitals is three and, therefore, the maximum number of electrons that can be accommodated in a set of p-orbitals is six, hence p-block contains six groups.

Boron Family

Group III A contains six elements: Boron, aluminium, gallium, indium, thallium and ununtrium. The penultimate shell (next to the outermost) conains $1s^2$ in boron, $2s^2\ 2p^6$ (8 electrons) in aluminium and $(n-1)s^2(n-1)p^6(n-1)d^{10}$ (18 electrons) in other elements.

Boron is a non-metal and always form covalent bonds. Boron family is known as most heterogeneous family as there is no regular trend in all properties, as it comes after d-block, lanthanoid contraction, poor shielding of d-orbital, they have large deviation in properties.

1. **Physical Properties**

   The atomic radius, ionic radius and density increases when one moves from top to bottom in a group in periodic table. While melting point decreases from B to Ga and then increases from (Ga to In). Ionisation energy decreases from B to Al, but shows a reverse trend in going from Al to Ga.

2. **Chemical Properties**

   i. **Reaction with air:** Impure boron in air forms oxide while pure boron is less reactive.

   $$4B + 3O_2 \longrightarrow 2B_2O_3$$

   ii. **Reaction with water:** Boron is not affected by water or steam under ordinary conditions. However, Aluminium reacts with cold water if oxide layer is not present on its surface.

   $$4Tl + 2H_2O + O_2 \longrightarrow 4TlOH$$

   iii. **Reaction with acids:** Boron is not affected by non-oxidising acids like HCl and dilute H_2SO_4 while other elements dissolve and liberate H_2 gas.

   $$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$

   iv. **Reaction with alkalies:** Boron, Aluminium, Gallium reacts with alkali solutions whereas Indium and Thallium are not affected by alkalies.

   $$2B + 6NaOH \longrightarrow 2Na2BO_3 + 3H_2$$

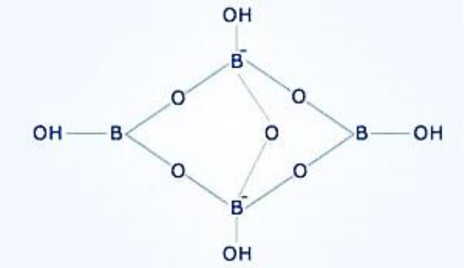
Anomalous Properties of Boron

Boron, the first member of group 13 elements, shows anomalous behaviour and differ from rest of the members of its family. The main reason for this difference is:

- Exceptionally small atomic and ionic size.
- High ionization enthalpy.
- Absence of d orbital in its valence shell.
- It has higher melting and boiling point than those of the other members of its group.

Borax

It Borax contains the tetranuclear unit i.e. $[B_4O_5(OH)_4]^{2-}$. The correct formula is $Na_2[B_4O_5(OH)_4].8H_2O$.



1) **From Tincal**

Naturally occurring borax is called tincal or suhaga. Tincal obtained from dried up lakes contains 50% borax. It is boiled with water and filtered to remove insoluble impurities of clay, sand. The filtrate is concentrated when crystals of borax separate out.

2) **From Colemanite**

The mineral colemanite is finely powdered and is boiled with sodium carbonate solution.

$$Ca_2B_6O_{11} + 2\,Na_2CO_3 \longrightarrow Na_2B_4O_7 + 2\,NaBO_2 + 2\,CaCO_3\downarrow$$

The precipitate of calcium carbonate thus formed is removed by filtration. The filtrate is concentrated and cooled when crystals of borax separate out. Sodium metaborate present in the mother liquor can be converted into borax by passing a current of carbon dioxide through it.

3) **From Boric Acid**

Borax can also be prepared in small amounts by neutralising boric acid with sodium carbonate.

On cooling crystal of borax i.e., $Na_2B_4O_7.10H_2O$ separate out.

Properties of Borax

1) It is a white crystalline solid, less soluble in cold water but more soluble in hot water.
2) The aqueous solution of borax is alkaline due to hydrolysis. Borax is therefore, used as a water softener and cleaning agent.

$$Na_2B_4O_7 + 2\,H_2O \longrightarrow 2\,NaOH + H_2B_4O_7$$

$$H_2B_4O_7 + 5\,H_2O \longrightarrow 4\,H_3BO_3$$

Action of heat- borax Bead Test

Borax loses its water of crystallisation and swells up to form a puffy mass. On further heating, it melts into a clear liquid which solidifies to a transparent glass like bead which consists of sodium metaborate ($NaBO_2$) and boric anhydride(B_2O_3)

$$Na_2B_4O_7.10H_2O \longrightarrow Na_2B_4O_7 + 10\,H_2O$$

$$Na_2B_4O_7 \longrightarrow 2\,NaBO_2 + B_2O_3$$

The glassy bead is commonly known as borax bead and is employed in qualitative analysis for the detection of certain coloured basic radicals such as Ni^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+}. Whenever a coloured salt containing these cations is heated with borax bead on a platinum wire, the salt decomposes to form the corresponding metal oxide which then combines with B_2O_3 present in the glassy bead to form coloured metaborates. This test is called borax bead test.

$$CoSO_4 \longrightarrow CoO + SO_3$$

$$CoO + B_2O_3 \longrightarrow Co\,(BO_2)_2$$

$$NiO + B_2O_3 \longrightarrow Ni(BO_2)_2$$

$$Cr_2O_3 + B_2O_3 \longrightarrow 2\ Cr(BO_2)_3$$

$$MnO + B_2O_3 \longrightarrow Mn(BO_2)_2$$

$$CuO + B_2O_3 \longrightarrow Cu(BO_2)_2$$

Action of Sodium Hydroxide

On adding a calculated quantity of sodium hydroxide to borax, sodium metaborate is formed.

$$Na_2B_4O_7 + 2\ NaOH \longrightarrow Na_2BO_2 + H_2O$$

Action of Sulphuric Acid

On adding a calculated quantity of concentrated sulphuric acid to a hot concentrated solution of borax, boric acid is produced.

$$Na_2B_4O_7 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2B_4O_7$$

$$H_2B_4O_7 + 5\ H_2O \longrightarrow 4\ H_3BO_3$$

Action of Ethyl Alcohol and Sulphuric Acid

On heating borax with ethyl alcohol and concentrated sulphuric acid, vapours of triethylborates are produced. When ignited these vapours burn with a green edged flame.

$$Na_2B_4O_7 + H_2SO_4 + 5\ H_2O \longrightarrow Na_2SO_4 + 4\ H_2BO_3$$

$$H_3BO_3 + 3\ C_2H_5OH \longrightarrow B\ (OC_2H_5)_3 + 3\ H_2O$$

Uses of Borax

Borax is used in:

1) in the manufacture of enamels and glazes for earthen ware. The glazed surface is resistant to heat, stains and scratches.
2) as a flux in soldering
3) in the preparation of medicinal soaps due to its antiseptic properties.
4) in the manufacture of heat resistant Borosilicate glass.
5) to make peroxyborate - an important cleansing and bleaching agent present in washing powder.
6) as a stiffening agent for candle wicks.
7) to produce a good finish in laboratory.
8) in the laboratory for borax bead test.
9) in softening of water.

Boron Hydrides

The binary compounds of boron with hydrogen are called Boron hydrides.

These hydrides of boron are called boranes.These hydrides can be divided into several series:

1) B_nH_{n+4} (called nido borane) such as B_2H_6 (diborane), B_5H_9 (pentaborane) , B_6H_{10} (hexaborane) , B_8H_{12} (octaborane) , $B_{10}H_{14}$ (decaborane).
2) B_nH_{n+6} (called arachno borane) such as B_4H_{10} (tetraborane) , B_5H_9 (pentaborane), B_6H_{10} (hexaborane), B_8H_{14} (octaborane), $B9H_{15}$ (nonaborane).

Preparation

1) By reduction of boron trifluoride etherate with Lithium aluminium hydride in diethyl ether.

$$4\ BF_3.Et_2O + 3\ LiAlH_4 \longrightarrow 2\ B_2H_6 + 3\ LiF + 3\ AlF_3 + 4\ Et_2O$$

2) Diborane is prepared in the laboratory by the oxidation of sodium borohydride with iodine in diglyme as solvent.

$$NaBH_4 + I_2 \longrightarrow B_2H_6 + 6\ NaF$$

3) On the industrial scale, diborane is obtained by the reduction of BF_3 with sodium hydride.

$$BF_3 + 6\ NaH \longrightarrow B_2H_6 + 6\ NaF$$

Preparation of higher boranes

Higher boranes are obtained when B_2H_6 is heated at 373-523 K.

Properties

1) **Physical state**

Diborane is a colourless ,highly toxic gas, b.p. 180 K.

2) **Stability**

Diborane is stable only at low temperature. When diborane is heated in a sealed tube, between 373- 533 K, a complex reaction occurs and various higher boranes are formed.

$$B_2H_6 \longrightarrow B_4H_{10},\ B_5H_{11},\ B_6H_{12}$$

By careful control of temperature, pressure and reaction time, different individual boranes can be obtained.

$$2\ B_2H_6 \longrightarrow B_4H_{10} + H_2$$

3) **Combustibility**

It catches fire spontaneously upon exposure to air. It burns in oxygen evolving an enormous amount of heat.

$$B_2H_6 + 3\ O_2 \longrightarrow B_2O^3 + 3\ H_2O\ ;\ \Delta_cH^\circ = -1976\ KJ/mol$$

Like diboranes, higher boranes spontaneously burn in air.

4) **Hydrolysis**

Boranes are readily hydrolysed by water to form boric acid.

$$B_2H_6 + 6\ H_2O \longrightarrow 2\ H_3BO_3 + 6\ H_2$$

With methanol, trimethylborate is formed.

$$B_2H_6 + 6\ CH_3OH \longrightarrow 2\ B\ (OCH_3)_3 + 6\ H_2$$

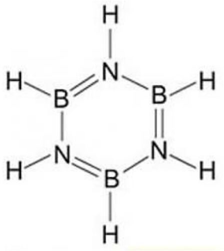
5) **Reaction with Lewis bases – cleavage reaction**

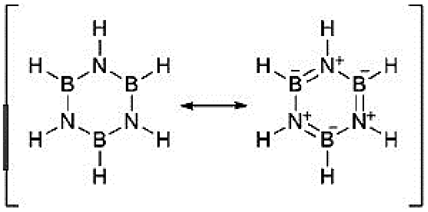
Diborane on treatment with Lewis bases first undergoes cleavage to form borane which then reacts with Lewis bases to form adducts.

$$B_2H_6 + 2\ NMe_3 \longrightarrow 2\ BH_3.NMe_3$$

$$B_2H_6 + 2\ CO \longrightarrow 2\ BH_3.CO$$

6) **Reaction with Ammonia**





Diborane combines with ammonia to form an addition product, $B_2H_6.2NH_3$ formulated as $[BH_2(NH_3)_2]^+$ $[BH_4]^-$, which when heated to 473 K decompose to give a volatile compound called borazine or borazole.

$$3\ B_2H_6 + 6\ NH_3 \longrightarrow 3\ [BH_2(NH_3)_2]^+[BH_4]^- \longrightarrow 2\ B_3N_3H_6 + 12\ H_2$$

Borazine is isoelectronic and isosteric with benzene and its structure is similar to that of benzene expect that in benzene the π-electrons are completely delocalised but in borazine, they are only partially delocalized.

Because of its similarity with benzene, borazine is also called inorganic benzene.

7) Formation of complex borohydride

Several metal hydrides react with diborane to from tetrahydridoborates known as borohydride. All these contain the tetrahedral $[BH_4]^-$ ion.

$$2\ NaH + B_2H_6 \longrightarrow 2\ Na^+[BH_4]^-$$

$$2LiH + B_2H_6 \longrightarrow 2\ Li^+[BH_4]^-$$

Both sodium borohydride and lithium borohydride are used as reducing agent in organic synthesis. They also serve as starting material for many other borohydrides.

8) Reaction with alkalies

Diborane dissolves in strong alkali to produce metaborates and dihydrogen gas.

$$B_2H_6 + 2\ KOH + 2\ H_2O \longrightarrow 2\ KBO_2 + 6\ H_2$$

9) Action of halogen acids

Diborane reacts with halogen acids to give halodiboranes evolving H_2 gas.

The reactivity of halogen acids follows the order: HI> HBr > HCl

Thus, HI react at about 323 K in absence of catalyst while HBr and HCl reacts in presence of their aluminium halide as catalyst.

$$B_2H_6 + HI \longrightarrow B_2H_5I + H_2$$

$$B_2H_6 + HBr \longrightarrow B_2H_5Br + H_2$$

$$B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2$$

10) Action of halogens

Halogens also react with diborane to form the corresponding halodiboranes.

The reactivity decreases in the order: $Cl_2 > Br_2 > I_2$.

Thus, Cl_2 reacts explosively at room temperature, Br2 reacts rapidly at 373 K while I_2 reacts slowly at still higher temperature.

$$B_2H_6 + Cl_2 \longrightarrow B_2H_5Cl + HCl$$

Uses of Boron Hydrides

1) Dibornae is used for preparing a number of boron hydrides such as $LiBH_4$, $NaBH_4$.
2) It is used as a reducing agent in organic reactions.
3) It is used as a fuel for supersonic rockets.

Structure of Diborane

1) In diborane, each boron atom has 3 Valence electrons for sharing. If we assume that each boron forms 3 covalent bonds with 3 hydrogen atoms, then there are no electrons left with boron atom for sharing with other boron atoms. Therefore, the two boron atoms cannot be linked.

   There are two types of hydrogen atom:

1) The four hydrogen atoms (two on left and two on right shown by thick lines) are called terminal hydrogens.

   These four terminal hydrogens and the two boron atoms lie in the same plane while the remaining two hydrogen atoms- one lying above and one lying below this plane form bridges and hence are called which bridged hydrogen.

Bana are two types of bonds in B_2H_6 molecules.

1) The four terminal B-H bonds are normal covalent bonds and hence are quite strong. Each bond is formed by sharing a pair of electron between B and H and hence are also called two centre electron pair bonds or two centre two electron bond (2c - 2e)
2) The two bridge bonds i.e. B—–H—–B are quite different from normal covalent bonds. Each bridge hydrogen is bonded to two boron atoms by a pair of of electrons. These are three centre electron pair bonds or three centre 2 electron bonds and hence are quiet weak.

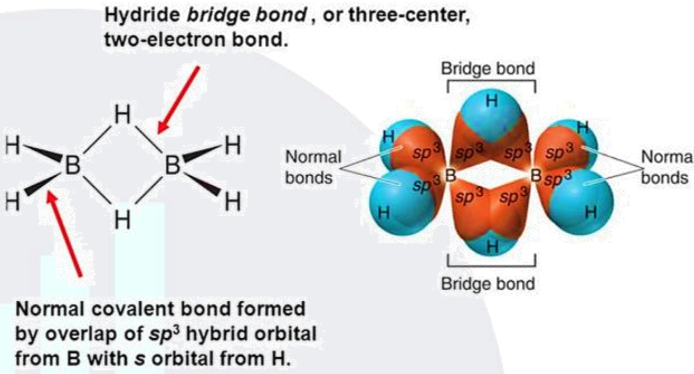
Because of their semblance to a banana, these three centre electron pair bonds are also called banana Bond.

Structure of diborane on the basis of hybridization

The boron atom in the excited state is $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^0$.

It undergoes sp^3 hybridisation

The two half-filled hybrid orbitals of each boron atom overlap with the half-filled orbitals of hydrogen atom forming normal covalent bonds whereas the third half-filled hybrid orbital of one boron atom and the vacant hybrid orbital of the second boron atoms overlap simultaneously with the half-filled orbitals of hydrogen atom The electron cloud contains only two electrons but spreads over 3 atoms. That is why this bond is called three centre electron pair bond.



Hydride *bridge bond*, or three-center, two-electron bond.

Normal covalent bond formed by overlap of sp^3 hybrid orbital from B with s orbital from H.

Because of the shape of the electron cloud formed, it is called banana bond. Molecules like B_2H_6 which do not have sufficient number of electrons to form normal covalent bonds are called electron deficient molecules.

Compounds of Boron

1. **Borax/ Sodium Tetraborate ($Na_2B_4O_7{\cdot}10H_2O$)**

   It is the most important compound of boron. It is a white crystalline solid. Borax dissolves in water to give an alkaline solution.

   Preparation:

   From Boric acid: Boric acid is neutralised with sodium carbonate and the resulting solution is cooled to get crystals of borax.

$$H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + H_2O + CO_2$$

   Properties:

   i. It gets hydrolysed with water to form an alkaline solution

$$Na_2B_4O_7 + 7H_2O \longrightarrow 2NaOH + H_3BO_3$$

   ii. **Borax bead test:** On heating borax first swells up due to elimination of water molecules. On further heating it melts to a liquid which then solidifies to a transparent glassy mass.

$$Na_2B_4O_7.10H_2O \longrightarrow Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 \longrightarrow 2NaBO_2 + B_2O_3$$

   iii. It is a useful primary standard for titration against acids.

$$Na_2[B_4O_5(OH)_4]{\cdot}8H_2O + 2HCl \longrightarrow 2NaCl + 4H_3BO_3 + 5H_2O$$

2. **Diborane: B_2H_6**

   The simplest boron hydride known, is diborane. It is prepared by treating boron trifluoride with $LiAlH_4$ in diethyl ether.

Preparation

$$3LiAlH_4 + 4BCl_3 \longrightarrow 3LiCl + 3AlCl_3 + B_2H_6$$

Properties

i. Stable at low temperature only, colourless and highly toxic.

ii. $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$

iii. $B_2H_6 + 6Cl_2 \longrightarrow 2BCl_3 + 6HCl$

iv. $B_3H_6 + 2Me_3N \longrightarrow 2[Me_3N.BH_3]$

Uses of Boron and Aluminium and their Compounds

Boron Compounds

Boron is a hard solid having high melting point low density and very low electrical conductivity. Some important boron compounds are:

1. **Boron fibers:** It is mixed with plastic to form a material which is lighter than aluminium but tougher and stiffer than steel hence it is used in body armour, missiles and aircrafts.
2. **Boron-10 (^{10}B) isotope:** Boron carbide rods or boron steel are used to control nuclear reactions as neutron absorbers.

$$_5B^{10} + {_0n^1} \longrightarrow {_5B^{11}}$$

3. **Borax:** It is used in manufacture of enamels and glazes for pottery and tiles. It is also used in making optical glasses and also borosilicate glasses which is very resistant to heat and shock. It is used as an antispectic.
4. **Boric acid:** It is used in glass industry, in food industry as preservative. It is also used as an antiseptic and eye wash under the name 'boric lotion'. It is also used in manufacture of enamels and glazes for pottery.
5. **Boron carbide:** Hardest boron compound.

Aluminium Compounds

Aluminium and its alloy are used in packing industry, utensil industry, aeroplane and transportation industry etc.

1. **Alumina ($Al2O_3$):**
   a) Used in chromatography.
   b) Used in making bauxite bricks which are used for lining furnaces.
2. **Aluminium chloride ($AlCl_3$):** Used in manufacture of dyes, drugs and perfumes and also in manufacture of gasoline. It is also used as catalyst in Friedel Craft reaction.
3. **Potash Alum. [K_2SO_4-$Al_2(SO_4)_3$-24 H_2O]:** Used in purification of water, leather tanning, as antiseptic and as a mordant.

Group 14 Elements: The Carbon Family

Group IV A contains six elements: carbon, silicon, germanium, tin, lead and ununquadium. The penultimate shell (prior to outermost) contains $1s^2$ -grouping in carbon, $2s^22p^6$ (8 electrons) in silicon and $(n-1)s^2(n-1)p^6(n-1)d^{10}$ (18 electrons) in other elements. This shows why carbon differs from silicon in some respects and these two differ from rest of the members of this group. General electronic configuration is ns^2np^2.

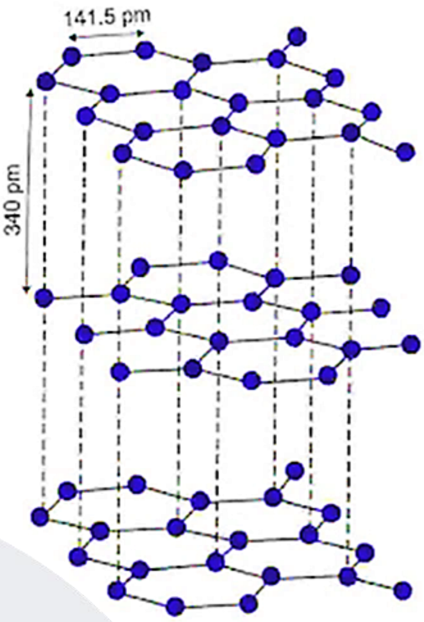
1. Atomic and Physical Properties

The important properties of carbon family are discussed below:

i. **Atomic Radii:** The atomic radii of group 14 elements are less than the corresponding elements of group 13. However, the atomic radii increase down the family.

ii. **Ionisation Energies:** The higher ionisation energies than group 13 are due to the higher nuclear charge and smaller size of atoms of group 14 elements. While moving down the group, the ionisation energies decrease till Sn.

$$C > Si > Ge > Sn < Pb$$



iii. **Oxidation state and valency:** The elements of group 14 show tetravalency by sharing four of its valence electrons. Therefore, they have oxidation state of +4. In addition, Ge, Sn and Pb also show +2 oxidation state.

iv. **Catenation:** Catenation is ability of like atoms to link with one another through covalent bonds. Tendency decreases from C to Pb. It is due to the decreasing M-M single bond energy. Thus, the tendency for catenation decreases as:

$$C > Si > Ge > Sn > Pb$$

v. **Allotropy:** All the elements of the carbon family with the exception of lead exhibit allotropy. Carbon exists as two important allotropic forms diamond and graphite.

2. **Chemical Properties**

i. **Reactivity towards air:** All members of this group form monoxide of the general formula MO such as CO, SiO, SnO and PbO. All members of this group form dioxides of molecular formula MO_2 such as CO_2, SiO_2, GeO_2, SnO_2 and PbO_2.

ii. **Reactivity towards water:** In this family three members i.e., carbon, silicon and germanium are affected by water while lead is not affected by water due to formation of protective oxide film, but tin decomposes with steam into tin dioxide and hydrogen gas.

iii. **Reactivity towards halogen:** These elements form two types of hallides - MX_2 and MX_4. Most of the MX_4 are covalent. SnF_4 and PbF_4 are ionic in nature.

Anomalous Behaviour of Carbon

Carbon shows anomalous behaviour due to its smaller size, higher electronegativity, higher ionization enthalpy and unavailability of d orbitals. Carbon atom forms double or triple bonds involving pπ-pπ bonding. Carbon has also the property to form closed chain compounds with O, S and N atoms as well as forming pπ-pπ multiple bonds with other elements particularly N, S and O. When we move down the group size increases and electronegativity decreases hence catenation tendency decreases. Order is:

$C >> Si > Ge \approx S$

Allotropes of Carbon

Carbon shows allotropism due to catenation and pπ-pπ bond formation. Carbon exists in two allotropic forms – crystalline and amorphous. The crystalline forms are diamond and graphite while the amorphous forms are coal, charcoal and lamp-black. The third form is fullerenes discovered by Kroto, Smalley and Curl.

Note: Tin has maximum number of allotropes.

Diamond

In diamond each carbon is joined to other four carbon tetrahedrally and carbon-carbon bond length is 1.54Å and bond angle is 109°28′ having sp3 hybridisation on each carbon. All four electrons in carbon are involved in bonding hence, it is bad conductor of electricity. Diamond is an excellent thermal conductor.

It is hardest natural substance known. It is transparent and has a specific gravity 3.52 and its refractive index is high (2.45). Difficult to break due to extented covalent bonding. Diamond is used for making cutters. Blades of diamond are used in eye surgery and as an abrasive for sharpening hard tools. Impure diamonds (black) are used in knives for cutting glass.

Graphite

Each carbon is sp^2 hybridised. It has layered structure. These layers are attracted by van der Waals force. Each carbon has one free electron in p-orbital, so it is a good conductor of electricity. All electrons get delocalized in one layer and form π-bond. Electron jumps from one orbital to another hence it is a good conductor of heat and electricity. In graphite carbon-carbon bond length is 141.5 pm and distance between adjacent graphite layer is 340 pm.

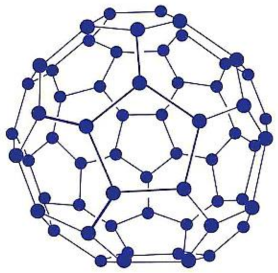
Graphite is used as a lubricant at high temperature. Oil gets burn or denatured at high temperature but graphite does not get denatured even at high temperature so, preferred over oil and grease.

Fullerene

It was made as a result of action of a laser beam or strong heating of a sample of graphite in presence of inert atmosphere. The sooty material mainly contains C_{60} with C_{70} (small amount). Most common fullerene is C_{60} called Buckminsterfullerene which has football-like structure. It contains 20 six-membered ring and 12 five-membered ring. It is used to make ball bearings.

Coal

It is the crude form of carbon. It has been formed in nature as a result of slow decomposition of vegetable matter under the influence of heat, pressure and limited supply of air. The successive stages of transformation are peat, lignite, bituminous, steam coal and anthracite. Bituminous is hard stone, burns with smoky flame. The superior quality is anthracite which burns with non-smoky flame.



Uses of carbon

- **Graphite:** In making lead pencils, electrodes of electric furnances, as a moderator in nuclear reactor, as a lubricant in machinery.
- **Charcoal:** In removing offensive odour from air, in removing fused oil from crude spirit, in decolourising sugar syrup, in gas masks etc.
- **Carbon black:** For making printing inks, black paints, Indian inks, boot polishes and ribbons of typewriters.
- **Coal:** For the manufacture of coal gas, coal tar, coke, and synthetic petrol.

Allotropes of Carbon

1. **Carbon Monoxide (CO)**

   Preparation: Carbon monoxide is majorly prepared by

   $$2C + O_2 \longrightarrow 2CO$$

   Properties:

   i. Burns with blue flame

   $$2CO + O_2 \longrightarrow 2CO_2$$

   ii. $CO + Cl2 \longrightarrow COCl_2$ (Phosgene)

   iii. $CO + 2H_2 \longrightarrow CH_3OH$

   iv. Many of the transition metals form metal carbonyls

   $$Ni + 4CO \longrightarrow Ni(CO)_4$$

2. **Carbon Dioxide (CO_2)**

   Preparation:

   Carbon dioxide is mostly prepared by decomposition of carbonates and bicarbonates:

   i. $CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$

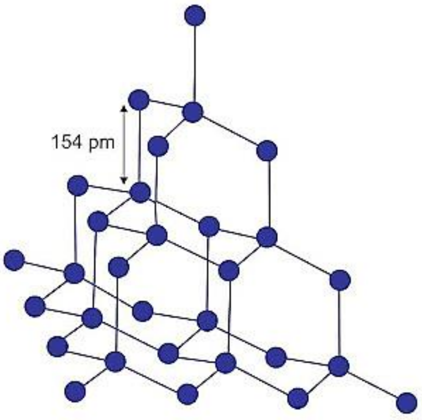
   ii. $CaCO3 \longrightarrow CaO + CO2$

   Properties:

   Carbon dioxide is an acidic, colourless gas. The important properties are:

   i. $Zn + CO_2 \longrightarrow ZnO + CO$

   ii. $2Mg + CO_2 \longrightarrow 2MgO + C$



iii. $2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$

iv. $Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$

Silicones

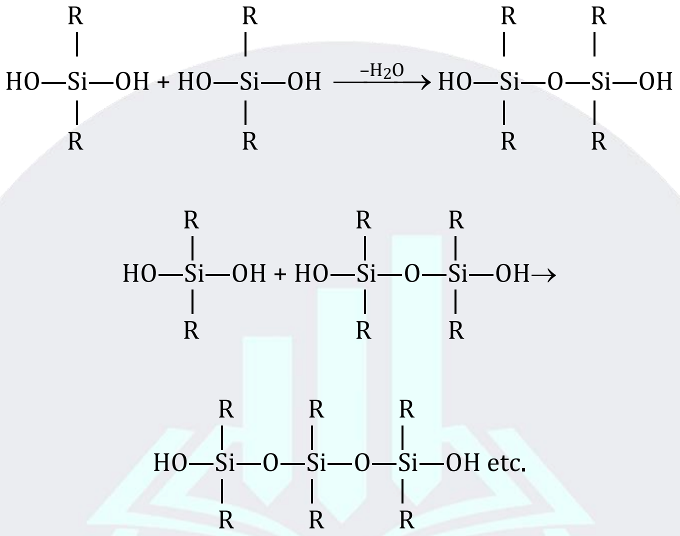
Silicones are synthetic organosilicon polymers containing repeated R_2SiO units held by Si-O-Si linkages.

These compounds have general formula $(R_2SiO)_n$ where R = methyl or aryl group.

Preparation

When methyl chloride reacts with silicon in the presence of copper as a catalyst at 570 K , various types of methyl substituted chlorosilanes of formula CH_3SiCl_3 , $(CH_3)_2SiCl_2$, $(CH_3)_3SiCl$ along with small amount of $(CH_3)_4Si$ are formed.

Hydrolysis of dichlorodimethylsilanes followed by polymerization yields chain polymers.



$$\mathrm{HO{-}\underset{R}{\overset{R}{Si}}{-}OH + HO{-}\underset{R}{\overset{R}{Si}}{-}OH \xrightarrow{-H_2O} HO{-}\underset{R}{\overset{R}{Si}}{-}O{-}\underset{R}{\overset{R}{Si}}{-}OH}$$

$$\mathrm{HO{-}\underset{R}{\overset{R}{Si}}{-}OH + HO{-}\underset{R}{\overset{R}{Si}}{-}O{-}\underset{R}{\overset{R}{Si}}{-}OH \rightarrow}$$

$$\mathrm{HO{-}\underset{R}{\overset{R}{Si}}{-}O{-}\underset{R}{\overset{R}{Si}}{-}O{-}\underset{R}{\overset{R}{Si}}{-}OH\ etc.}$$

Properties

1) Silicones made up of short chain molecules are oily liquid, silicones with medium chains behave as viscous oils, jellies and greases, those with very long chains behave as rubbery elastomers and resins.
2) They are chemically inert i.e. resistant to oxidation, thermal decomposition or to attack by organic reagents.
3) Silicones being surrounded by non-polar alkyl group are water repelling in nature.
4) They are heat resistant and have high dielectric strength i.e., have good electrical insulating properties.

Uses

1) For making water proof papers, wool, textile, wood by coating them with a thin film of silicone.
2) As sealants and electrical insulators.
3) As lubricant at high as well as low temperature since there is little change in their viscosities with temperature.
4) Being biocompatible, they are used in surgical and cosmetic implants.

Summary-

1. **Allotropes:** Those compounds which have different physical properties but similar chemical properties are called allotropes e.g., diamond and graphite.
2. **Catenation:** Tendency of carbon atom to link with itself to form long chain is called catenation.
3. **Inert pair effect:** Decrease in tendency of ns^2 electron pair to participate in bond formation with increase in atomic number is called inert pair effect.
4. **Silicones:** It is organosilicon compound containing repeated R_2SiO units.
5. **Silicates:** Compounds in which anions are either discrete SiO_4^{-4} units or a number of such units combine

together through corners.

6. **Alums:** All double sulphates having one monovalent basic radical and one trivalent basic radical.
7. **Boranes:** Hydrides of boron are called as boranes.

Class : 11th Chemistry
Chapter- 11: p - Block Elements

p - Block Elements

Group 13 Elements

[B, Al, Ga, In, Tl]

Electronic configuration: ns^2np^1

Atomic Radii: Atomic radius of Ga is less than Al.

I.E.: Decrease from B to Al is associated with increase in size. $\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3$

Electronegativity: Down the group, decreases from B to Al and then increases marginally.

Physical Properties:

- Non-metallic, hard and black coloured solid.
- Exists in many allotropic forms.
- B has high m.p. while others have low m.p.
- Density increases down the group.

Chemical Properties:

- Oxidation State: +1, +3

$2E_{(s)} + 3O_{2(g)} \xrightarrow{\Delta} 2E_2O_{3(s)}$

$2E_{(s)} + N_{2(g)} \xrightarrow{\Delta} 2EN_{(s)}$

$2Al_{(s)} + 6HCl_{(aq)} \longrightarrow 2Al^{3+}{}_{(aq)} + 6Cl^-_{(aq)} + 3H_{2(g)}$

$2E_{(s)} + 3X_{2(g)} \longrightarrow 2EX_{3(s)} \quad (X = F, Cl, Br, I)$

Trends and Anomalous Properties of Boron:

- Except in boron, $[M(OH)_4]^-$ and $[M(H_2O)_6]^{3+}$ exist in aqueous medium.
- Boron trifluoride reacts with Lewis bases.
- Maximum covalence of B is 4.

Important Compounds of Boron:

(i) Borax $(Na_2B_4O_7 . 10H_2O)$ White crystalline solid

$Na_2B_4O_7 + 7H_2O \longrightarrow 2NaOH + 4H_3BO_3$

$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$

Borax bead test is used for identification.

(ii) Orthoboric acid (H_3BO_3): White crystalline solid, soapy touch

Preparation Properties: $Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4B(OH)_3$

$B(OH)_3 + 2HOH \longrightarrow [B(OH)_4]^- + H_3O^+$

$H_3BO_3 \xrightarrow{\Delta} HBO_2 \xrightarrow{\Delta} B_2O_3$

(iii) Diborane (B_2H_6)

Preparation: $4BF_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3LiF + 3AlF_3$

$2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$

$2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$

Properties: Colourless, toxic, b.p.: 180K, catches fire

$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O \qquad \Delta_CH^\theta = -1976 KJ mol^{-1}$

$B_2H_6(g) + 6H_2O(l) \longrightarrow 2B(OH)_{3(aq)} + 6H_{2(g)}$

$B_2H_6 + 2NMe_3 \longrightarrow 2BH_3.NMe_3$

$B_2H_6 + 2CO \longrightarrow 2BH_3CO$

$3B_2H_6 + 6NH_3 \longrightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\Delta} 2B_3N_3H_6 + 12H_2$

Uses of Boron and Aluminium and their Compounds:

- Boron fibers are used in making bullet-proof vest and light material for aircraft.
- Borax is used in manufacturing heat resistant glasses.
- Al is used in packing, utensil making, construction and transportation industry.

Group 14 Elements

[C, Si, Ge, Sn, Pb]

Electronic configuration: $ns^2 np^2$

Covalent Radius: Increase from C to Si and from Si to Pb a small increase is observed.

I.E.: Decreases down the group.

Electro negativity: More than group 13 elements. From Si to Pb same.

Physical Properties:

- Solid.
- C and Si are non- metals, Ge metalloid, Sn and Pb are soft metals.
- M.p. and b.p. higher than group 13 elements.

Chemical Properties:

- Oxidation State: +4, +2
- Forms oxides on heating in oxygen.
- C, Si, Ge, and Pb are not affected by water.

$Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_2$

- Form halides of formula MX_2 and MX_4

Important Trends and Anomalous Behavior of Carbon:

- C differs from rest due to smaller size, higher electronegativity, high ionisation enthalpy and unavailability of d orbitals.
- C forms $p\pi$–$p\pi$ multiple bonds
- Shows Catenation

Allotropes of Carbon:

- Diamond
- Carbon
- Fullerenes

Uses of Carbon:

- Graphite composites are used in tennis rackets, fishing rods, aircrafts and canoes.
- Graphite is used for electrodes in batteries and industrial electrolysis.
- C black is used in black ink and as filter in automobile tyres.
- Diamond is used in jewellry.

Important Compounds of C and Si

Zeolites: used as catalyst in petrochemical industries.

Silicon Dioxide: Si is covalently bonded to 4 oxygen atoms.

Silicates Structural 4- unit is $SiO_4{}^4$

Silicones: Group of organosilicon polymers (R_2SiO) with replanting unit.

Carbon Dioxide:

$C + O_2 \xrightarrow{\Delta} CO_2$

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

Carbon monoxide:

$2C + O_2 \xrightarrow[Limited\ air]{\Delta} 2CO$

$HCOOH \xrightarrow[Conc.H_2SO_4]{373K}$

$H_2O + CO$

Electronic configuration:

$ns^2np^{1\text{-}6}$ (except He)

Producer Gas: Mixture of $CO+N_2$

Water Gas: or Synthesis Gas:
Mixture of $CO+H_2$

Important Questions

Multiple Choice questions-

1. Consider the following statement about Ozone I. 03 is formed by the interaction of fluorine. II. It turns tetramethyl base paper as violet. III. It turns benzidine paper as brown. The correct set of true statement is
   (a) I and II
   (b) I, II and III
   (c) I and III
   (d) II and III
2. In the compound of type ECl3, where E = B, P, As, or Bi, the angle Cl – E – Cl for different E are ion the order:
   (a) B = P = As = Bi
   (b) B > P > As > Bi
   (c) B < P = As = Bi
   (d) B < P < As < Bi
3. In white phosphorous(P_4) molecule, which one is not correct:
   (a) 6P-P single bonds are present
   (b) 4P-P single bonds are present
   (c) 4 lone pair of electrons is present
   (d) P-P-P bond angle is 60°
4. All the elements of oxygen family are
   (a) Non metals
   (b) Metalloids
   (c) Radioactive
   (d) Polymorphic
5. Which of the following will not produce hydrogen gas?
   (a) Reaction between Fe and dil. HCl
   (b) Reaction between Zn and NaOH
   (c) Reaction between Zn and conc. H_2SO_4
   (d) Electrolysis of NaCl in Nelsons cell
6. Amorphous form of Silica is
   (a) Tridymite
   (b) Kieselguhr
   (c) Cristobalite
   (d) Quartz
7. Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behavior is that graphite.
   (a) Has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interpolate bonds
   (b) Is a non – crystalline substance
   (c) Is an allotropic from of carbon
   (d) Has molecules of variable molecular masses like polymers.
8. Borax is used as a cleansing agent because on dissolving in water, it gives
   (a) Alkaline solution
   (b) Acidic solution
   (c) Bleaching solution
   (d) Amphoteric solution.
9. Among the C-X bond (where, X = Cl, Br, I) the correct decreasing order of bond energy is
   (a) C–I > C–Cl > C–Br
   (b) C–I > C–Br > C–Cl
   (c) C–Cl > C–Br > C–I
   (d) C–Br > C–Cl > C–I
10. On heating boron with caustic potash, the pair of products formed are
    (a) Potassium Borate + Dihydrogen
    (b) Potassium Borate + Water
    (c) Potassium Borate + H_2
    (d) Borax + Dihydrogen.
11. Which of the following statements regarding ozone is not correct?
    (a) The oxygen-oxygen bond length in ozone is identical with that of molecular oxygen
    (b) The ozone is response hybrid of two structures
    (c) The ozone molecule is angular in shape
    (d) Ozone is used as a germicide and disinfectant for the purification of air.
12. There is no S-S bond in
    (a) $S_2O^{2-}4$
    (b) $S_2O^{2-}5$
    (c) $S_2O^{2-}3$
    (d) $S_2O^{2-}7$

13. Which is strongest Lewis's acid?
    (a) BF_3
    (b) BCl_3
    (c) BBr_3
    (d) BI_3
14. Fertilizer having the highest nitrogen percentage is:
    (a) Calcium cyanamide
    (b) Urea
    (c) Ammonium nitrate
    (d) Ammonium sulphate
15. In general, the Boron Trihaides act as
    (a) Strong reducing agent
    (b) Lewis Acids
    (c) Lewis Bases
    (d) Dehydrating Agents

Very Short:

1. Do boron halides form additional compounds with amines?
2. How does boron interact with NaOH?
3. What is the oxidation state of C in
    (a) CO
    (b) HCN
    (c) H_2CO_3
    (d) CaC_2
4. What is the state of hybridization of C in
    (a) CO_3^{2-}
    (b) CCl_4
    (c) diamond
    (d) Graphite?

5. Give two examples of electron-deficient compounds.

6. Arrange the following halides of boron in the increasing order of acidic character
7. What is dry ice? Why is it so-called?
8. Write balanced equations to show hydrolysis reactions of CO_3^{2-} and HCO_3^{-}.
9. Why boron does not form B3+ ion?
10. Which oxide of carbon is an anhydride of carbonic acid?

Short Questions:

1. Although boric acid $B(OH)_3$ contains three hydroxyl groups, yet it behaves as a monobasic acid. Explain.
2. $SiCl_4$ forms $[SiCl_6]^{2-}$ while CCl4 does not form $[CCl_6]^{2-}$ Explain.
3. Why does not silicon form an analogue of graphite?
4. Why carbon forms covalent compounds whereas lead forms ionic compounds?
5. How is borax prepared from?
6. Mention three important uses of borax.

Long Questions:

1. SiCl. forms $[SiCl]^{2-}$ while CClL does not form $[CCl]^{2-}$. Explain
2. Borazine is more reactive than benzene. Why?
3. (i) What are the different oxidation states exhibited by the group 14 elements? Discuss the stability of their oxidation states.
    (ii) What type of oxides are formed by group 14 elements? Which of them are acidic, neutral or basic?
4. (a) $[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ is not known. Give reasons
    (b) Select the member (s) of group 14 that
        (i) forms the most acidic oxide
        (ii) is commonly found in the +2-oxidation state
        (iii) used as a semi-conductor.
    (c) Explain why a diamond that is covalent has a high melting point?
    (d) Discuss the reaction of silica with
        (i) NaOH
        (ii) HE
5. (a) Carbon exhibits catenation, whereas silicon does not. Explain.
    (b) How does boron differ from aluminum.
    (c) Write the similarities between boron and silicon.

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

    Assertion (A): If Aluminium atoms replace a few silicon atoms in three-dimensional network of silicon dioxide, the overall structure acquires a negative charge.

    Reason (R): Aluminium is trivalent while silicon is tetravalent.

    (i) Both A and R are correct and R is the correct explanation of A.

(ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): Silicon's are water repelling in nature.

   Reason (R): Silicon's are organosilicon polymers, which have (–R2SiO–) as repeating unit.

   (i) A and R both are correct and R is the correct explanation of A.

   (ii) Both A and R are correct but R is not the correct explanation of A.

   (iii) A and R both are not true.

   (iv) A is not true but R is true.

Case Study Based Question:

1. The heavier members of 13 and 14 groups besides the group oxidation state also show another oxidation state which is two units less than the group oxidation state. Down the group (↓), the stability of higher oxidation state decreases and that of lower oxidation state increases. This concept which is commonly called inert pair effect has been used to explain many physical and chemical properties of the element of these groups.

(1) Heavier members of groups 13 exhibit oxidation state

(a) +3 only

(b) +1 only

(c) +1 and +3 both

(d) +1, +2, +3

(2) Which among the following is the strongest oxidising agent?

(a) SiO_2

(b) GeO_2

(c)SnO_2

(d) PbO_2

(3) Which among the following is the strongest reducing agent?

(a) GaCl

(b) InCl

(c) BCl_3

(d) TlCl

(4) The strongest reductant among the following is

(a) $SnCl_2$

(b) $SnCl_4$

(c) $PbCl_2$

(d) $GeCl_2$

(5) Which of the following statement is wrong?

(a) Tl(III) salt undergo disproportionation.

(b) CO is used as a reducing agent.

(c) CO_2 is a greenhouse gas.

(d) SiO_2 is a covalent solid.

Answer Key

MCQ

1. (b) I, II and III
2. (b) B > P > As > Bi
3. (a) 6P-P single bonds are present
4. (d) Polymorphic
5. (c) Reaction between Zn and conc. H_2SO_4
6. (c) Cristobalite
7. (a) Has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interpolate bonds
8. (a) Alkaline solution
9. (c) C–Cl > C–Br > C–I
10. (a) Potassium Borate + Dihydrogen
11. (a) The oxygen-oxygen bond length in ozone is identical with that of molecular oxygen
12. (d) $S_2O^{2-}_7$
13. (a) BF_3
14. (b) Urea
15. (b) Lewis Acids

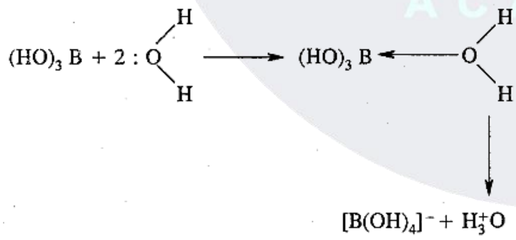
Very Short Answer:

1. Boron halides are Lewis's acids and hence accept a pair of electrons from amines to form additional compounds.
2. 2B + 6NaOH → 2Na3BO3 + 3H2.
3. (a) + 2
   (b) +2
   (c) +4
   (d) -1
4. (a) sp^2
   (b) sp^3
   (c) sp^3
   (d) sp^2
5. BF_3 and B_2H_6.
6. $BF_3 < BCl_3 < BBr_3 < BI_3$.
7. Solid CO_2 is known as dry ice. It does not wet a piece of paper/cloth and sublimes without melting. Therefore, it is called dry ice.
8. $CO3^{2-} + H_2O \rightleftharpoons OH^- + HCO^{3-}$

   $HCO_3^- + H_2O \rightleftharpoons OH^- + H_2CO_3$.
9. Boron has a very high sum of the first three ionisation enthalpies. Hence it cannot lose three electrons to form a B^{3+} ion.
10. CO_2, because H_2CO_3 acid decomposes to give H_2O and CO_2.

Short Answer:

1. **Ans:**



Hydrated species

$B(OH)_3$ is not a protonic acid.

It behaves as a Lewis acid because it abstracts a pair of electrons from hydroxyl ion.

2. **Ans:** Carbon does not have d-orbitals and hence C. Cl_4 does not combine with Cl^- ions to give $[CCl_6]^{2-}$, On the other hand, silicon has vacant 3d-orbitals and thus can expand its covalency from 4 to 6. Therefore, $SiCl_4$ combines with CL ions to form $[SiCl_6]^{2-}$

$$SiCl_4 + 2Cl^- \rightarrow [SiCl_6]^{2-}$$

3. **Ans:** In graphite, C is sp^2 hybridised and each C is linked to three other C atoms forming hexagonal rings. Thus, graphite has a two-dimensional sheet-like structure.

   Silicon, on the other hand, does not form an analogue of C because of the following two reasons:

   1. Silicon has a much lesser tendency for catenation than C as Si-Si bonds are much weaker than C-C bonds.
   2. Silicon because of its larger size than C undergoes sp3 hybridisation.

4. **Ans:** Carbon cannot lose electrons to form C4 because the sum of four ionisation enthalpies is very high. It cannot gain four electrons to form C4 because energetically it is not favorable. Hence C forms only covalent compounds. Down the group 14, ionisation enthalpies decrease, Pb being the last element has so low I.E. that it can lose electrons to form ionic compounds.

5. **Ans: (I)** Borax is also called sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$). It can be prepared as follows:

   From colemanite: Powdered mineral is boiled with sodium carbonate solution and filtered. The filtrate is concentrated and then cooled when crystals of borax.

$Ca_2B_6O_{11} + 2Na_2CO_3 \rightarrow Na_2B_4O_7 + 2NaBO_2 + 2CaCO_3$.

   The mother-liquor which contains sodium meta-borate is treated with a current of C02, to convert it into borax which separates out.

$$4NaBO_2 + CO_2 \rightarrow Na_2B_4O_7 + Na_2CO_3$$

(ii) **From Tincal:** Tincal obtained from dried up lakes is boiled with water. The solution is filtered to get rid of insoluble impurities of clay, sand etc. The filtrate is concentrated to get the crystals of borax.

(iii) **From boric acid:** Boric acid is neutralised with sodium carbonate and the resulting solution is concentrated and cooled to get the crystals of borax $Na_2B_4O_7.10H_2O$.

$$4H_3BO_3 + Na_2CO_3 \rightarrow Na_2B_4O_7 + 6H_2O + CO_2 \uparrow$$

6. **Ans:** It is used:
   - As a flux soldering and welding in industry.
   - In the manufacture of borosilicate glass (or pyrex glass).
   - In making enamels and glazes.
   - In stiffening of candle wicks.

- In softening of water.
- In a qualitative analysis for borax bead test in the laboratory.

Long Answer:

1. **Ans:** Carbon does not have d-orbitals, hence CCl_4 does not combine with Cl ions to form $[CCl_6]^{2-}$. On the other hand, silicon has vacant 3-d orbitals & thus $SiCl_4$ combines with Cl^- ions to form

[Sicy2-

$SiCl_4 + 2Cl^- \rightarrow [SiCl_6]^{2-}$

In other words, carbon shows a fixed covalency of 4 but silicon exhibits varying covalency from 4 to 6.

2. **Ans:** Both Borazine & Benzene are isoelectronic. In benzene C = C bonds are non-polar while N=B bonds in borazine are polar in nature due to the presence of a co-ordinate bond between N & B atoms. As a result, addiction is quite frequent in borazine while it is less in benzene because of delocalization of π-electron charge.

3. **Ans:**

(i) The group 14 elements have four electrons in the outermost shell. The common oxidation states exhibited by these elements are +4 and +2. Since the sum of the first four ionisation enthalpies is very high, compounds in the +4-oxidation state are generally covalent in nature. In heavier members such as Ge, Sn and Pb, the tendency to show +2 oxidation state increases. It is due to the inability of ns2 electrons of the valence shell to participate in bonding.

The relative stabilities of these two oxidation states vary down the group. C and Si mostly show a +4-oxidation state. Ge forms stable compounds in the +4 state and only a few compounds in the +2 state. Sn forms compounds in both oxidation states (Sn in +2 state is a reducing agent).

Lead compounds in the +2 state are stable and in the +4 state are strong oxidising agents. In the tetravalent state, the number of electrons around the central atom in a molecule (e.g., carbon in CCl_4) is eight. Being electron precise molecules, they are normally not expected to act as an electron acceptor or electron donor.

Although carbon cannot exceed its covalence of more than 4, other elements of the group can do so. It is because of the presence of d-orbital in them. Due to this, their halides undergo hydrolysis and have a tendency to form complexes by accepting electron pairs from donor species. For example, the species like SiF_5^-, SiF_6^-, $[GeCl_6]^{2-}$, $[Sn(OH)_6]^{2-}$ exist where the hybridisation of the central atom is sp^3d^2.

(ii) All members when heated in oxygen form oxides. There are -mainly two types of oxides, i. e., monoxide and dioxide of formula MO and MO_2 respectively. SiO only exists at high temperature. Oxides in the higher oxidation state of elements are generally more acidic than those in the lower oxidation state. The dioxides-CO_2, SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

4. **Ans:**

(a) (i) $[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ does not exist.

The main reasons are (i) six large chlorine atoms cannot be accommodated around silicon atom due to the limitation of their size.

(ii) Interactions between lone pairs of a chlorine atom and silicon atom are not very strong

(b) (i) The most acidic dioxide is formed by carbon (CO_2).

(ii) Lead is mostly found in the +2 oxidation state in its compounds.

(iii) Silicon and germanium are used as semiconductors.

(c) Though diamond has covalent bonding in it, yet it has a high melting point, because a diamond has a 3-dimensional network involving strong C—C bond, which are very difficult to break and in turn, it has a high melting point.

(d) (i) SiO_2 reacts with HF as follows:

$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$

(ii) SiO_2 reacts with HF as follows:

$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$.

5. **Ans:**

(a) Carbon shows catenation because of its smaller size, high bond energy of C – C bond, the possibility of sp, sp^2, sp^3 hybridisation and formation of multiple bonds C-C (1σ), C = C (1σ + S1π),- C = C (1σ + 2π). On the other hand, silicon shows only limited catenation because of its large atomic radius, low bond energy of Si-Si bond and absence of multiple bonds between Si atoms.

(b) Difference between boron and aluminum:

1. Boron is a non-metal but aluminum is a metal.
2. Boron is a semi-conductor while aluminum is a good conductor of electricity.
3. Boron forms a number of hydrides called boranes, but Al forms a polymeric hydride.
4. Halides of boron (except BF_3) are readily hydrolysed by water whereas halides of A1 are only partially hydrolysed by water.
5. B_2O_3 is acidic, but Al_2O_3 is amphoteric.
6. Boron hydroxide $B(OH)_3$ is acidic, but $Al(OH)_3$ is amphoteric.

(c) Similarities between boron and silicon:

1. Both are non-metals.
2. Both are semi-conductors
3. Boron and silicon form a number of covalent hydrides which have similar properties. For example, they spontaneously catch fire on exposure to air and are readily hydrolysed by water.
4. The halides of boron and silicon are readily hydrolysed by water.
5. Boron trioxide (B_2O_3) and silicon dioxide (SiO_2) are acidic in nature. These dissolve in alkali solution forming borates and silicates.

Assertion Reason Answer:

1. (i) Both A and R are correct and R is the correct explanation of A.
2. (ii) Both A and R are correct but R is not the correct explanation of A.

Case Study Answer:

1. **Answer:**

(1) (c) +1 and +3 both

(2) (d) PbO_2

(3) (c) BCl_3

(4) (d) $GeCl_2$

(5) (a) Tl(III) salt undergo disproportionation.

❖❖

Organic Chemistry Some Basic Principles and Techniques

12

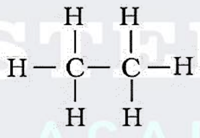
Introduction

In this chapter, we shall discuss some basic principles and techniques of analysis needed for understanding the formation and properties of organic compounds. Organic compounds are essential for existence and maintenance of life on earth. These include complex molecules like (DNA) which carry genetic information and proteins which is building blocks of life. Organic compounds also play an important role in material used in daily life such as cloths, fuel, dyes, and medicines etc.

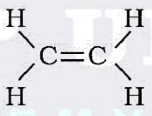
Structural Representations of Organic Compounds

Structural Formulas

The Lewis structures can be simplified by representing the two electron covalent bonds by a dash (–). In this representation, a single bond is represented by a single dash (–), a double bond by a double dash (=) and a triple bond by a triple dash (≡). The lone pair on an atom may or may not be shown. This representation is called structural formula.



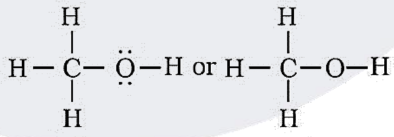
Ethane



Ethene

$H-C\equiv C-H$

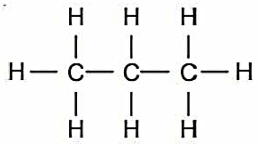
Ethyne



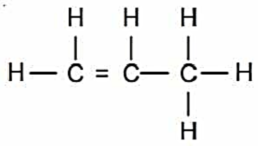
Methanol

Condensed Formulas

In this formula, the arrangement of atoms are shown but the bonds between may be omitted and the number of identical groups attached to an atom are indicated by a subscript.



may be represented as $CH_3-CH_2-CH_3$ or $CH_3CH_2CH_3$

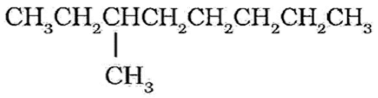


may be represented as $CH_2=CH-CH_3$

Condensed Formulas

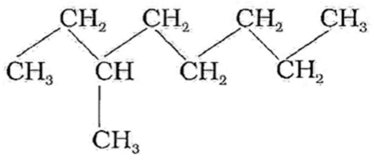
In this representation, the carbon and hydrogen atoms are not shown and the lines between carbon-carbon bonds are shown in a zig-zag manner.

(a)

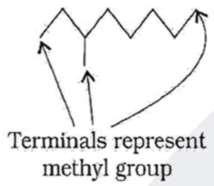


$CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_2CH_2CH_2CH_3$

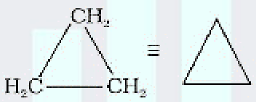
(b)



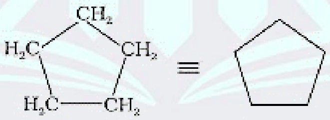
(c)



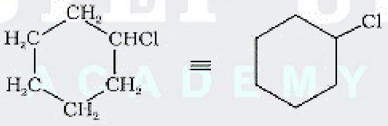
In cyclic compounds, the bond-line formulas may be given as follows:



Cyclopropane



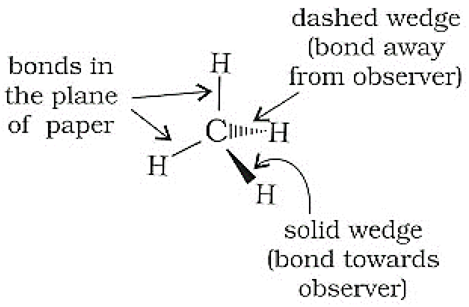
Cyclopentane



chlorocyclohexane

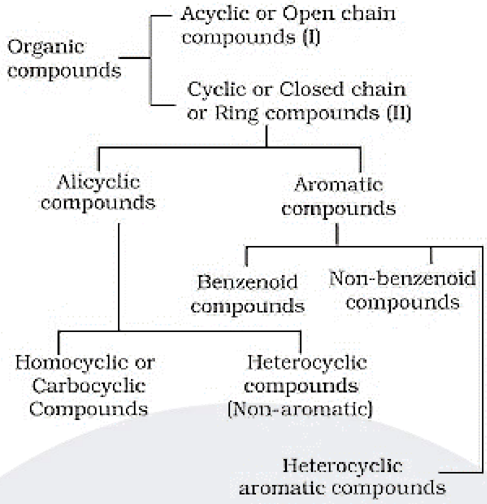
Three-dimensional representation of organic molecules

The three-dimensional (3-D) structure of organic molecules can be represented on paper by using certain conventions. In these formulae, the thick solid (or heavy) line or the solid wedge indicates a bond lying above the plane of the paper and projecting towards the observer while a dashed wedge is used to represent a bond lying below the plane of the paper and projecting away from the observer.



Classification of Organic Compounds

On the basis of their structures, organic compounds are broadly classified as follows:

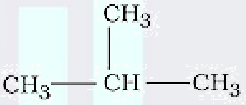


Open Chain Compounds

These compounds contain open chains of carbon atoms in their molecules. The carbon chains may be either straight chains or branched chains. They are also called aliphatic compounds.

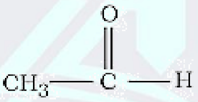
CH_3CH_3

Ethane



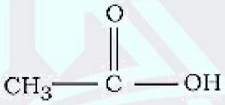
$CH_3-\overset{\overset{\Large CH_3}{|}}{C}H-CH_3$

Isobutane



$CH_3-\overset{\overset{\Large O}{\|}}{C}-H$

Acetaldehyde



$CH_3-\overset{\overset{\Large O}{\|}}{C}-OH$

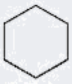
Acetic acid

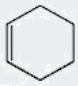
Closed Chain or Ring Compounds

These compounds contain chains or rings of atoms in their molecules.

Alicyclic Compounds: These compounds contain a ring of three or more carbon atoms in them. They resemble aliphatic compounds in many of their properties.


Cyclopropane

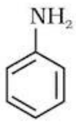

Cyclohexane

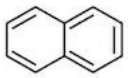

Cyclohexene

Aromatic Compounds: These have a cyclic system containing at last one benzene ring. The parent member of the family is called benzene. Benzene has a homocyclic hexagonal ring of six carbon atoms with three double bonds in the alternate positions.

Benzenoid aromatic compounds


Benzene

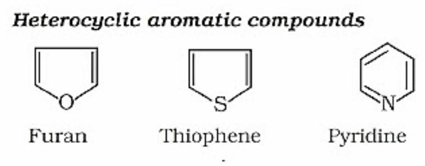

Aniline


Naphthalene

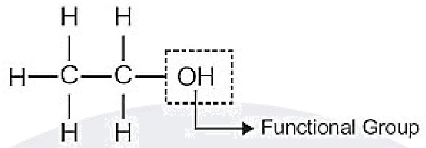
Non-benzenoid compound


Tropone

Heterocyclic Compounds: In these compounds, the ring contains one or more atoms of either nitrogen, oxygen or sulphur in addition to carbon atoms. The atom other than carbon (such as N, O, S) present in the ring is called hetero atoms.



Functional Groups: An atom or group of atoms which largely determines the properties of the organic compounds particularly the chemical properties.



Derivatives of Hydrocarbon

Homologous Series: Homologous series may be defined as "a series of similarly constituted compounds in which the members possess the same functional group and have similar chemical characteristics". The two consecutive members differ in their molecular formula by $-CH_2-$ group.

1. CH_3OH - Methyl alcohol
2. C_2H_5OH - Ethyl alcohol
3. C_3H_7OH - Propyl alcohol
4. C_4H_9OH - Butyl alcohol
5. $C_5H_{11}OH$ - Pentyl alcohol
6. $C_6H_{13}OH$ - Hexyl alcohol

Nomenclature of Organic Compounds

The term 'nomenclature' means the system of naming of organic compounds. There are two systems of nomenclature:

1. **Trivial or Common System**

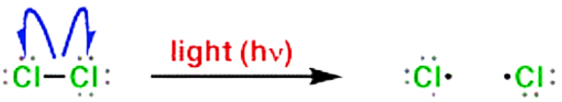
   In this nomenclature, the names of organic compounds were assigned based on their source of origin or certain properties. For instance, citric acid got its name from the source (citrus fruits) from which it was first isolated. Formic acid was named so as it was first obtained from red ant. In Latin ant word is formica.

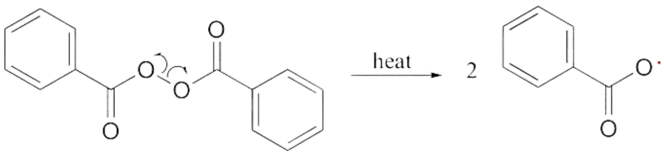
2. **IUPAC System of Nomenclature**

   A systematic method of naming has been developed and is known as the IUPAC (International Union of Pure and Applied Chemistry) system of nomenclature. In this systematic nomenclature, the names are correlated with the structure such that the reader or listener can deduce the structure from the name.

Free Radicals

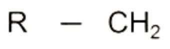
A free radical may be defined as an atom or a group having an odd or unpaired electron. These are generally produced by homolytic cleavage of a covalent bond.



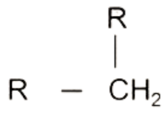


Classification of Free Radicals

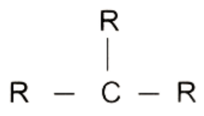
Free radicals are also classified as primary (1°), secondary (2°) and tertiary (3°) according as the carbon carrying the unpaired electron is primary, secondary and tertiary.



Primary (1⁰)



Secondary (2⁰)



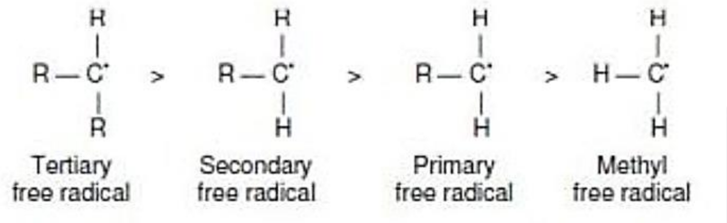
Tertiary (3⁰)

Stability of Free Radicals

The order of stability of free radicals is the same as that of carbocations i.e. 3° >2° >1°

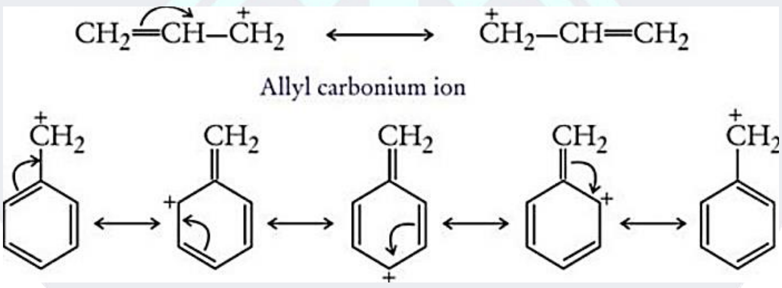
This order of stability can be explained on the basis of hyperconjugation.

Greater the number of alkyl groups attached to the carbon atom carrying the odd electrons, greater is the delocalization of the odd electrons and hence more stable is the alkyl free radical.



Stability of free radical

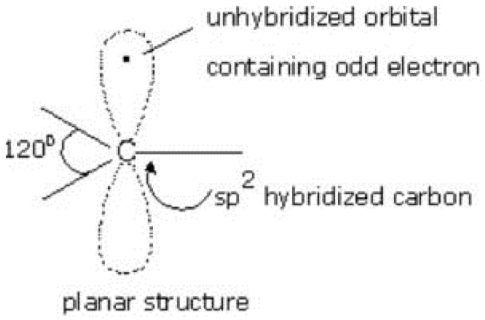
Allyl and benzyl free radicals are stabilized by resonance.



Greater the number of phenyl groups more stable is the free radical.

Free radicals are also very short-lived highly reactive chemical species because of the strong tendency of the carbon atom carrying the odd electron to acquire one more electron to complete its octet.

Orbital structure of Free Radicals



Alkyl free radicals are planar chemical species. In free radicals, the unhybridized p-orbital contains the odd electron.

Like carbanions, free radicals can also assume pyramidal shape since the energy difference between planar and pyramidal shape is not much.

Stereoisomerism

Isomers which have same structural formula but have different relative arrangement or atoms or groups in space are called stereoisomers and the phenomenon is called stereoisomerism.

cis-trans isomerism is an example of stereoisomerism.

cis-trans isomers

Due to π-bonding between the two carbon atoms, the rotation around carbon-carbon double bond is prohibited and hence the geometry of the atoms or groups attached to the carbon atoms gets fixed in space.

Stereoisomerism is also called geometrical isomerism.

Steric Hindrance

If two non-bonded atoms or groups in an organic molecule are held together at a distance equal to or less than the sum of their van der waal radii, then they repel each other due to spatial crowding. This repulsion is referred to as steric hindrance or steric strain or van der waal strains.

Molecules which possess steric strain are relatively less stable as compared to those having no steric strain.

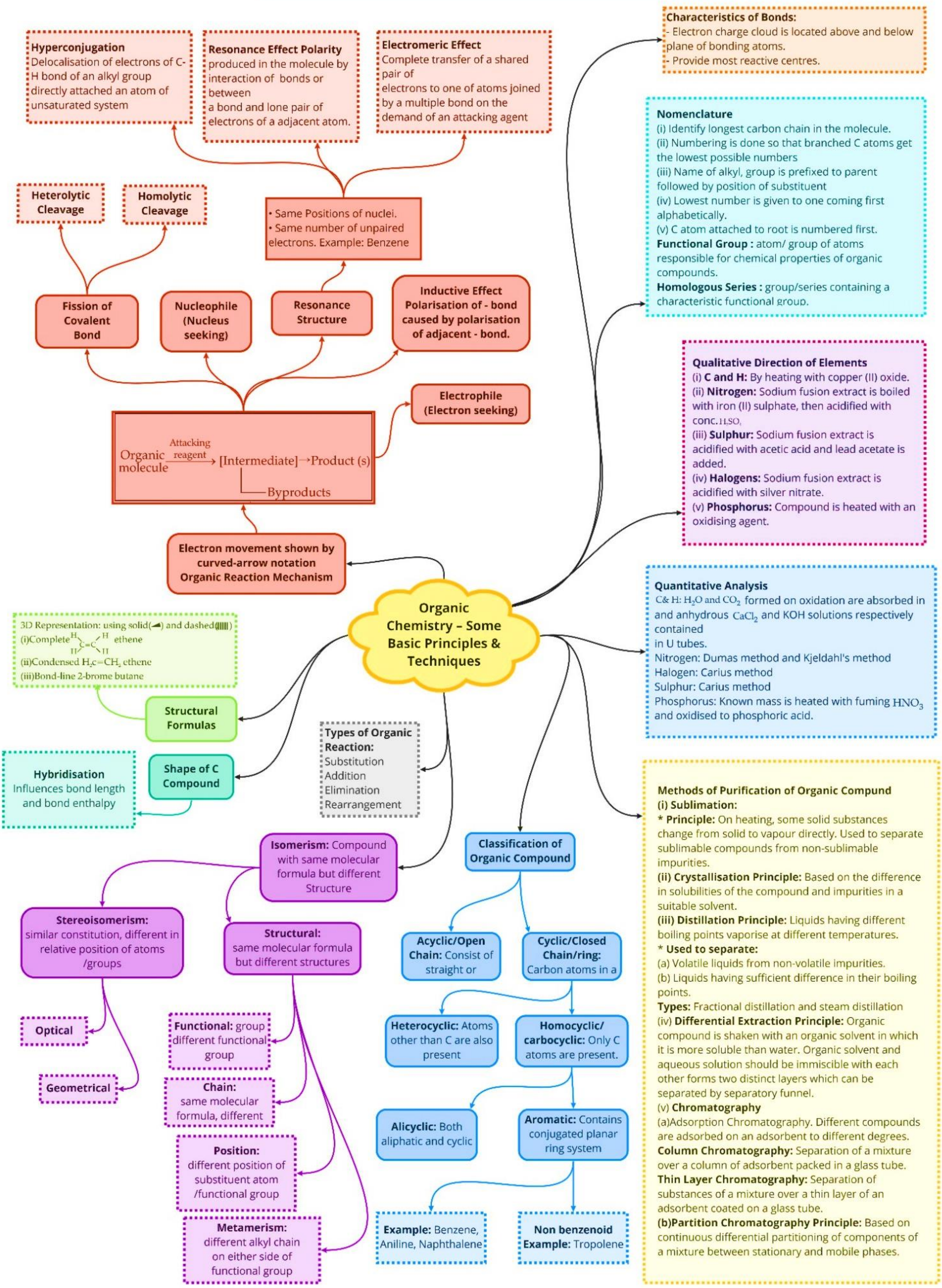
For Example: Cis-but-2-ene has steric hindrance and hence is less stable as compared to trans-but-2-ene which has no steric hindrance.

As the size of the atoms around a bulky atom increases, the steric hindrance increases accordingly.

Summary

1. **Condensed Structural Formula:** The structural formulae obtained by omitting some or all the covalent bonds and by indicating the number of identical groups attached to an atom by subscript is called condensed structural formula.
2. **Bond-line Structural Formula:** In this formula of organic compounds, carbon and hydrogen atoms are not shown and line representing C –C bonds and drawn in zig-zag fashion. The only atoms specifically written are those that are neither nor hydrogen bonded to carbon.
3. **Cyclic Compounds:** These are compounds in which carbon atoms are joined in rings i.e., they are closed chain compounds.
4. **Aromatic Compounds:** Benzene and its derivatives are called aromatic compounds.
5. Functional group: Functional group is an atom or group of atoms or reactive part of the compound which determines physical and chemical properties of compounds.
6. **Homologous Series:** Homologous series is a series of compounds which has same functional group same general formula and show gradation in physical and chemical properties of compounds.
7. **Isomerism:** The phenomenon of existence of two or more compounds possessing the same formula but different structural formula and different physical and chemical properties are called isomerism.
8. **Structural Isomerism:** Compounds having the same molecular formula but different structures are classified as structural isomers. Chain Isomerism: The isomers, which differ in carbon atom chain, are called chain isomers and this phenomenon is called chain isomerisms.
9. **Position Isomerism:** The isomers, which differ in position of substituent or functional groups are called position isomers and this phenomenon is called position isomerism.
10. **Functional Isomerism:** Those isomers, which differ in functional groups are called functional isomers and this phenomenon is called functional isomerism.
11. **Metamerism:** Those isomers, which differ in alkyl group attached with the di or tri valent atom of functional group. These are called metamers and this phenomenon is called metamerism.
12. **Stereoisomerism:** Those compounds that have the same composition and sequence of covalent bond but differ in relative positions of their atoms or groups in space.
13. **Free Radical:** An atom or group of atoms containing odd unpaired electrons in excited state is known as free radical.

Class : 11th Chemistry
Chapter- 12: Organic Chemistry – Some Basic Principles & Techniques



Organic Chemistry – Some Basic Principles & Techniques

Electron movement shown by curved-arrow notation Organic Reaction Mechanism

Organic molecule $\xrightarrow[\text{reagent}]{\text{Attacking}}$ [Intermediate] → Product (s)
Byproducts

Fission of Covalent Bond

Heterolytic Cleavage

Homolytic Cleavage

Nucleophile (Nucleus seeking)

Resonance Structure

- Same Positions of nuclei.
- Same number of unpaired electrons. Example: Benzene

Hyperconjugation
Delocalisation of electrons of C-H bond of an alkyl group directly attached an atom of unsaturated system

Resonance Effect Polarity
produced in the molecule by interaction of bonds or between a bond and lone pair of electrons of a adjacent atom.

Electromeric Effect
Complete transfer of a shared pair of electrons to one of atoms joined by a multiple bond on the demand of an attacking agent

Inductive Effect Polarisation of - bond caused by polarisation of adjacent - bond.

Electrophile (Electron seeking)

Structural Formulas

3D Representation: using solid(◢) and dashed(||||)
(i)Complete ethene
(ii)Condensed $H_2c=CH_2$ ethene
(iii)Bond-line 2-brome butane

Shape of C Compound

Hybridisation
Influences bond length and bond enthalpy

Types of Organic Reaction:
Substitution
Addition
Elimination
Rearrangement

Isomerism: Compound with same molecular formula but different Structure

Stereoisomerism: similar constitution, different in relative position of atoms /groups

Optical

Geometrical

Structural: same molecular formula but different structures

Functional: group different functional group

Chain: same molecular formula, different

Position: different position of substituent atom /functional group

Metamerism: different alkyl chain on either side of functional group

Classification of Organic Compound

Acyclic/Open Chain: Consist of straight or

Cyclic/Closed Chain/ring: Carbon atoms in a

Heterocyclic: Atoms other than C are also present

Homocyclic/ carbocyclic: Only C atoms are present.

Alicyclic: Both aliphatic and cyclic

Aromatic: Contains conjugated planar ring system

Example: Benzene, Aniline, Naphthalene

Non benzenoid **Example:** Tropolene

Characteristics of Bonds:
- Electron charge cloud is located above and below plane of bonding atoms.
- Provide most reactive centres.

Nomenclature
(i) Identify longest carbon chain in the molecule.
(ii) Numbering is done so that branched C atoms get the lowest possible numbers
(iii) Name of alkyl, group is prefixed to parent followed by position of substituent
(iv) Lowest number is given to one coming first alphabetically.
(v) C atom attached to root is numbered first.
Functional Group : atom/ group of atoms responsible for chemical properties of organic compounds.
Homologous Series : group/series containing a characteristic functional group.

Qualitative Direction of Elements
(i) **C and H:** By heating with copper (II) oxide.
(ii) **Nitrogen:** Sodium fusion extract is boiled with iron (II) sulphate, then acidified with conc.H_2SO_4
(iii) **Sulphur:** Sodium fusion extract is acidified with acetic acid and lead acetate is added.
(iv) **Halogens:** Sodium fusion extract is acidified with silver nitrate.
(v) **Phosphorus:** Compound is heated with an oxidising agent.

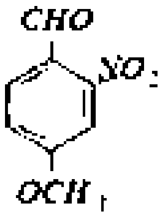
Quantitative Analysis
C& H: H_2O and CO_2 formed on oxidation are absorbed in and anhydrous $CaCl_2$ and KOH solutions respectively contained in U tubes.
Nitrogen: Dumas method and Kjeldahl's method
Halogen: Carius method
Sulphur: Carius method
Phosphorus: Known mass is heated with fuming HNO_3 and oxidised to phosphoric acid.

Methods of Purification of Organic Compund
(i) Sublimation:
* **Principle:** On heating, some solid substances change from solid to vapour directly. Used to separate sublimable compounds from non-sublimable impurities.
(ii) Crystallisation Principle: Based on the difference in solubilities of the compound and impurities in a suitable solvent.
(iii) Distillation Principle: Liquids having different boiling points vaporise at different temperatures.
* **Used to separate:**
(a) Volatile liquids from non-volatile impurities.
(b) Liquids having sufficient difference in their boiling points.
Types: Fractional distillation and steam distillation
(iv) **Differential Extraction Principle:** Organic compound is shaken with an organic solvent in which it is more soluble than water. Organic solvent and aqueous solution should be immiscible with each other forms two distinct layers which can be separated by separatory funnel.
(v) **Chromatography**
(a)Adsorption Chromatography. Different compounds are adsorbed on an adsorbent to different degrees.
Column Chromatography: Separation of a mixture over a column of adsorbent packed in a glass tube.
Thin Layer Chromatography: Separation of substances of a mixture over a thin layer of an adsorbent coated on a glass tube.
(b)Partition Chromatography Principle: Based on continuous differential partitioning of components of a mixture between stationary and mobile phases.

Important Questions

Multiple Choice questions-

1. Which among the following statement is not true?
   (a) In liquid, particles are less regularly arranged and are free to move
   (b) Boiling involves breaking up of group of molecules in liquid
   (c) Boiling involves separation of oppositely charged ions
   (d) Thermal energy of particles overcome cohesive forces that hold them
2. Identify the chiral molecule among the following:
   (a) Isopropyl alcohol
   (b) 2-pentanol
   (c) 1-bromo 3-butene
   (d) Isobutyl alcohol
3. Which element is estimated by Carius method?
   (a) Carbon
   (b) Hydrogen
   (c) Halogen
   (d) Nitrogen
4. A solution of (+) – 2 – chloro – 2 – phenylethane in toluene racemises slowly in the presence of small amounts of SbCl5 due to the formation of
   (a) Carbanion
   (b) Carbene
   (c) Free radical
   (d) Carbocation
5. Which of the following acids has the smallest dissociation constant?
   (a) $CH_3CHFCOOH$
   (b) FCH_2CH_2COOH
   (c) $BrCH_2CH_2COOH$
   (d) $CH_3CHBrCOOH$
6. What is the correct IUPAC name of?



   (a) 4-methoxy-2-nitrobenzaldehyde
   (b) 4-formyl-3-nitro anisole
   (c) 4-methoxy-6-nitrobenzaldehyde
   (d) 2-formyl-5-methoxy nitrobenzene
7. 0.5 g of hydrocarbon gave 0.9 g water on combustion. The percentage of carbon in hydrocarbon is
   (a) 75.8
   (b) 80.0
   (c) 56.6
   (d) 28.6
8. 0.92 g of an organic compound was analysed by combustion method. The mass of the U- tube increased by 1.08 g. What is the percentage of hydrogen in the compound?
   (a) 13.04%
   (b) 52.17%
   (c) 65.21%
   (d) 11.30%
9. What is the state of hybridisation of carbon in carbanion?
   (a) sp
   (b) sp^2
   (c) sp^3
   (d) sp^2d.
10. An organic compound contains C = 38.8 H = 16 and N = 45.2. Empirical formula of the compound is
    (a) CH_3NH_2
    (b) CH_3CN
    (c) C_2H_5CN
    (d) $CH_2(NH)_2$
11. 59 g of an amide obtained from a carboxylic acid, RCOOH, liberated 17 g of ammonia upon heating with alkali. The acid is
    (a) Formic Acid
    (b) Acetic Acid
    (c) Propionic Acid
    (d) Benzoic Acid

12. The displacement of electrons in a multiple bond in the presence of attacking reagent is called
    (a) Inductive effect
    (b) Electrometric effect
    (c) Resonance
    (d) Hyper conjugation
13. The molecular formula C_5H_{12} contains how many isomeric alkanes?
    (a) 1
    (b) 2
    (c) 3
    (d) 4
14. If two compounds have the same empirical formula but different molecular formula, they must have
    (a) Different percentage composition
    (b) Different molecular weight
    (c) Same viscosity
    (d) Same vapour density
15. Inductive effect involves
    (a) Displacement of σ electrons
    (b) Delocalization of π electrons
    (c) delocalization of σ-electrons
    (d) Displacement of π-electrons

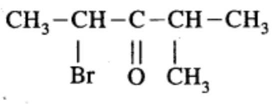
Very Short:

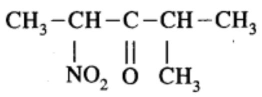
1. What type, of hybridisation, is involved in
   (i) planar and
   (ii) linear molecules?
2. Arrange the following in increasing order of C – C bond strength:

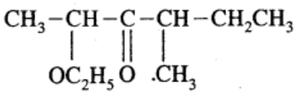
   C_2H_6, $C_2H_4C_2H_2$
3. Arrange the following in decreasing order of C — C bond length:
4. What is the type of hybridisation of C atoms in benzene?
5. What are isomers?
6. Select electrophiles out of the following:

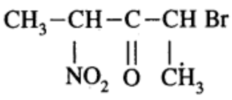
   H^+ Na^+, Cl^-, C^2HSOH, $AlCl^3$, SO^3, CN^-, $CH^3CH^2{+}$,: CCl^2, R-X.
7. Select nucleophiles from the following.

   BF_3 NH3 OH^-, R-X, C_2H_5OH, H_3O^+, NO_2, CN^-.
8. Give the I.U.P.A.C. names of the following compounds

(i)

$CH_3-\underset{Br}{CH}-\underset{O}{\overset{}{C}}-\underset{CH_3}{CH}-CH_3$

(ii)

$CH_3-\underset{NO_2}{CH}-\underset{O}{C}-\underset{CH_3}{CH}-CH_3$

(iii)

$CH_3-\underset{OC_2H_5}{CH}-\underset{O}{C}-\underset{CH_3}{CH}-CH_2CH_3$

(iv)

$CH_3-\underset{NO_2}{CH}-\underset{O}{C}-\underset{CH_3}{CH}\,Br$

(v) $(CH_3)_4C$

(vi) $(CH_3)_2CHCOOH$.

9. What is a functional group?
10. Arrange the following in increasing order of-I effect.

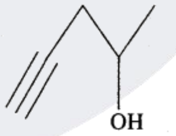
    (i) $-NO_2$, -COOH, -F, -CN, – I.

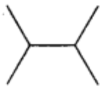
Short Questions:

1. Expand each of the following bond-line formulae to show all the atoms including carbon and hydrogen.

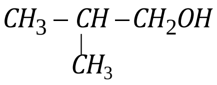
(a)

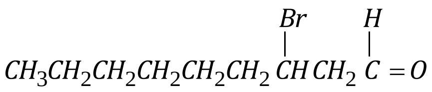

(b)

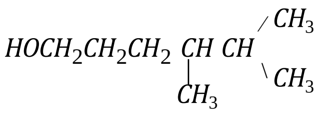

(c)


(d)


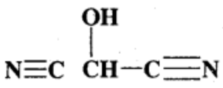
2. For each of the following compounds, write a more condensed and also their bond line formulae.

(a)

$CH_3-\underset{CH_3}{CH}-CH_2OH$

(b)

$CH_3CH_2CH_2CH_2CH_2CH_2\,\overset{Br}{CH}\,CH_2\,\overset{H}{C}=O$

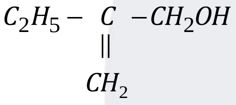
(c) 

$HOCH_2CH_2CH_2\underset{\underset{CH_3}{|}}{CH}\,CH\begin{smallmatrix}/\,CH_3\\ \backslash\,CH_3\end{smallmatrix}$

(d) 

$N\equiv C\ \overset{\overset{OH}{|}}{CH}-C\equiv N$

3. What is the type of hybridisation of each carbon in the following compounds?
   - (a) CH_3Cl
   - (b) $(CH_3)_2CO$
   - (c) CH_3CN
   - (d) $HCONH_2$
   - (e) $CH_3CH = CHCN$.
4. What is the shape of the following molecules:
   - (a) $H_2C = O$
   - (b) CH_3F
   - (c) $H\text{-}C \equiv N$?
5. Give the I.U.P. A.C. names of the following compounds:

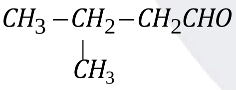
   (i) 

   $C_2H_5-\underset{\underset{CH_2}{||}}{C}-CH_2OH$

   (ii) $CH_3 - CH = CH\,COOH$

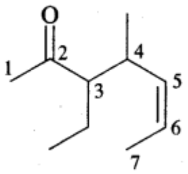
   (iii) $(CH_3)_2C = CHCOCH_3$

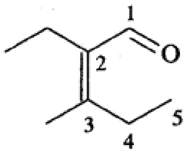
   (iv) 

   (v) 

   $CH_3-\underset{\underset{CH_3}{|}}{CH_2}-CH_2CHO$

   (vi) $CH_2 = CH - CN$.
6. Write the I.U.P.A.C. names of

   (i) 

   (ii) 

Long Questions:

1. Explain the principle of steam distillation.
2. Dehydrobromination of compounds (A) and (B) yield the same alkene (c) Alkene (c) Can regenerate (A) and (B) by the addition of HBr in the presence and absence of peroxide respectively. Hydrolysis of A and B give isomeric products (D) and (E) respectively. 1, 1-Diphenyl ethane is obtained on the reaction of (C) of benzene in the presence of H+ ions. Give structures of A to E with reactions.
3. What are reaction intermediates? How are they generated by bond fission?
4. 0.395 g of an organic compound by various method for the estimation of sulphur gave 0.582g of $BaSO_4$. Calculate the percentage of Sulphur.
5. 0.15g of an organic compound gave 0.12g of AgBr by carius method. Find the percentage of bromine in the compound.

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): Simple distillation can help in separating a mixture of propan-1-ol (boiling point 97°C) and propanone (boiling point 56°C).

   Reason (R): Liquids with a difference of more than 20°C in their boiling points can be separated by simple distillation.

   (i) Both A and R are correct and R is the correct explanation of A.

   (ii) Both A and R are correct but R is not the correct explanation of A.

   (iii) Both A and R are not correct.

   (iv) A is not correct but R is correct.
2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): Energy of resonance hybrid is equal to the average of energies of all canonical forms.

   Reason (R): Resonance hybrid cannot be presented by a single structure.

   (i) Both A and R are correct and R is the correct explanation of A.

   (ii) Both A and R are correct but R is not the correct explanation of A.

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

Case Study Based Question:

1. Read the passage given below and answer the following questions:

The electron displacements due to the influence of an atom or a substituent group present in the molecule cause permanent polarisation of the bond (called electronic effect), e.g.

$$CH_3 — \overset{\delta\delta+}{CH_2} — \overset{\delta+}{CH_2} — \overset{\delta-}{F}.$$

In above example, polar C—F bond induce polarity in the adjacent bonds. Such polarisation of adjacent σ- bond is referred to as the inductive effect. This effect decreases rapidly as the number of intervening bonds increases. The resonance effect is defined as the polarity produced in the molecule by the interaction of two π-bonds or in conjugated system.

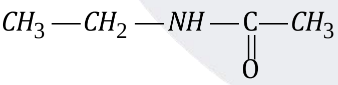
When the group or atom release electron density then electron density of conjugated system increases while the group or atom attract/withdraw electron density then electron density of conjugated system decreases.

(1) In which molecule dipole moment is the maximum?

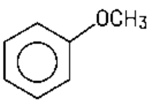
(a) $CH_3CH_2CH_2 — Cl$

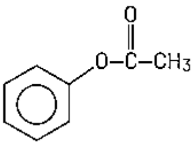
(b) $CH_3CH_2CH_2 — NO_2$

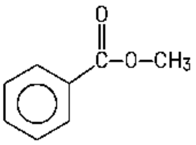
(c) $CH_3CH_2CH_2 — OH$

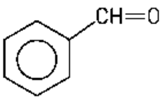
(d) 
$CH_3 — CH_2 — NH — \underset{\underset{O}{\|}}{C} — CH_3$

(2) In which benzene ring electron density is maximum?

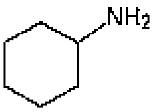
(a) 

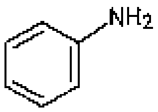
(b) 

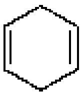
(c) 

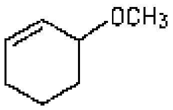
(d) 

(3) Which of the following system show abnormal behaviour in their properties (like-stability, polarity ... etc.)?

(a) 

(b) 

(c) 

(d) 

(4) The permanent displacement of electron through a chain involving only σ-bonds is called

(a) Inductive effect

(b) Hyperconjugation effect

(c) Electrometric effect

(d) Mesmeric effect

2. Read the following passage and answer the question accordingly.

An intermediate is a molecular entity, that is formed from the reactants and reacts further to give the directly observed products of a chemical reaction. Most chemical reactions are stepwise, that is they take more than one elementary step to complete. An intermediate is the reaction product of each of these steps, except for the last one, which forms the final very isolated. Also, owing to the short lifetime, they do not remain in the product mixture.

In certain cases, they are separated and stored. For example, matrix isolation and low temperature. Matrix isolation is a technique that is used experimentally in physics and chemistry that includes a material that has been trapped within an unreactive material. Host matrix generally comprises guest particles that are generally embedded. Guest particles can be molecules, atoms and ions. The guest is isolated within the host matrix.

(1) Relative stabilities of the following carbocations will be in the order

$$\underset{(A)}{\overset{\oplus}{C}H_3}, \underset{(B)}{CH_3\overset{\oplus}{C}H_2}, \underset{(C)}{\overset{\oplus}{C}H_2OCH_3}$$

(a) C > B > A

(b) C < B < A

(c) B > C > A

(d) C > A > B

(2) CH_3 CH_2 Cl undergoes homolytic fission, produces.

(a) $CH_3\overset{\bullet}{C}H_2$ and $\overset{\bullet}{Cl}$

(b) $CH_3\overset{\oplus}{C}H_2$ and Cl^-

(c) $CH_3\overset{\oplus}{C}H_2$ and $\overset{\oplus}{Cl}$

(d) $CH_3\overset{\bullet}{C}H_2$ and Cl^-

(3) The shape of carbocation is:

(a) square planar

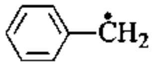
(b) trigonal planar

(c) octahedral

(d) trigonal pyramidal

(4) Compare stability of free radicals.

I. $CH_3 - \overset{\bullet}{C}H_2 - CH_3$

II. 

III. $\overset{\bullet}{C}H_2 - CH(CH_3)_2$

IV. $\overset{\bullet}{C}H_2 - CH_3$

(a) II > I > III > IV

(b) II > I > IV > III

(c) I > II > III > IV

(d) IV > III > I > II

Answer Key

MCQ

1. (c) Boiling involves separation of oppositely charged ions
2. (d) Isobutyl alcohol
3. (c) Halogen
4. (d) Carbocation
5. (c) $BrCH_2CH_2COOH$
6. (a) 4-methoxy-2-nitrobenzaldehyde
7. (b) 80.0
8. (a) 13.04%
9. (c) sp^3
10. (a) CH_3NH_2
11. (b) Acetic Acid
12. (b) Electrometric effect
13. (c) 3
14. (b) Different molecular weight
15. (a) Displacement of σ electrons

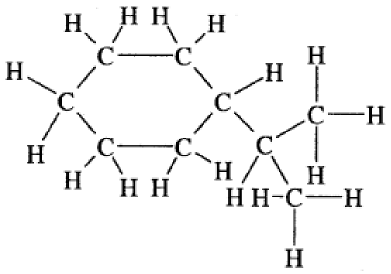
Very Short Answer:

1. (i) sp^2 (ii) sp.
2. $C_2H_6 < C_2H_4 < C_2H_2$.
3. $C_2H_6 > C_2H_4 > C_2H_2$.
4. It is an sp^2 type of hybridisation.
5. Compounds having the same molecular formula, but different physical and chemical properties are called isomers.
6. H^+, Na^+, A1Cl3, SO3, CH3CH$_2$+,: CCl$_2$, R-X.
7. NH_3, OH, C_2H_5OH, CN
8. (i) 2-Bromo-4 – methyl pent-3- one
   (ii) 4-Methyl-2-nitro pent – 3 – one
   (iii) 2 – Ethoxy – 4 – methoxypent – 3 – one
   (iv) 2-Bromo-4-nitro pent-3-one
   (v) 2, 2-Dimethylpropane
   (vi) 2-Methyl propanoic acid.
9. The atom or group of atoms present in a molecule that determines its chemical properties is called the functional group.
10. -I < -F < -COOH < -CN <NO_2.

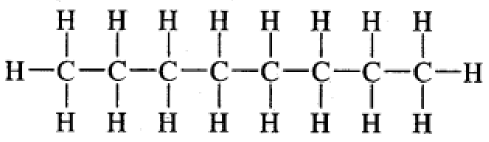
Short Answer:

1. Ans:

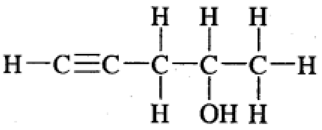
(a)



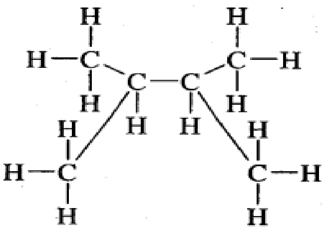
(b)



(c)



(d)

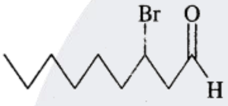


2. Ans:

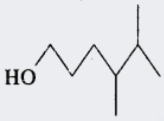
(a) Condensed formulae are

$(CH_3)2CH\ CH_2\ OH$

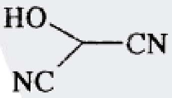
(b) $CH_3(CH_2)_5\ CHBr\ CH_2\ CHO$



(c) $HO(CH_2)_3\ CH(CH_3)\ CH(CH_3)_2$



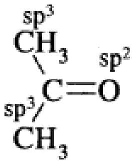
(d) $HOCH(CN)_2$



3. Ans:

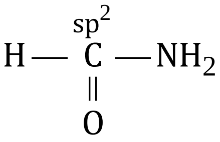
(a) $\overset{sp^3}{CH_3}-Cl$

(b)



(c) $\overset{sp^3}{CH_3}-\overset{sp}{C}\equiv N$

(d)

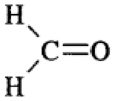


$H-\overset{sp^2}{\underset{\underset{O}{\|}}{C}}-NH_2$

(d) $\overset{sp^3}{CH_3}-\overset{sp^2}{CH}=\overset{sp^2}{CH}-\overset{sp}{C}\equiv N$

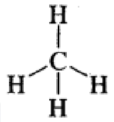
4. Ans:

(a) In $H_2C = O$; C is sp^2 hybridised, hence its shape is H trigonal planar



(b) In CH_3F -F; C is sp3 hybridized

∴ it is tetrahedral



(c) In H-C ≡ N; C is sp-hybridized, hence HCN is linear

H—C ≡ N.

5. Ans:

(i) 2-Ethylprop-2-en-l-ol

(ii) But-2-en-l-oic acid

(iii) 4-Methylpent-3-en-2-one

(iv) 3-Chloropropanal

(v) 3-Methylbutane-l-al

(vi) Prop-2-en-1-nitrile.

6. Ans:

(i) 3-Ethyl-4-methylhept-5-en-2-one

(ii) 2-Ethyl-3-methylpent-2-en-1 -one.

Long Answer:

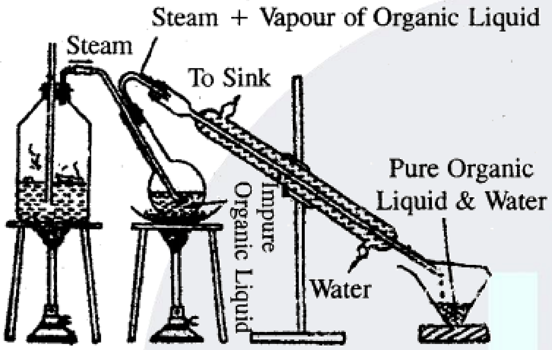
1. Ans: Steam distillation: The process of steam distillation is employed in the purification of substance from non-volatile impurities provided the substance itself is volatile in steam and insoluble in water.

This method is based on the facts that

1. A liquid boil at a temperature when its vapour pressure becomes equal to the atmospheric pressure.
2. The vapour pressure of a mixture of two immiscible liquids is equal to the sum of the vapour pressures of the individual liquids.

In the actual process, steam is continuously passed through the impure organic liquid. Steam heats the liquid and it gets practically condensed to water. After some time, mixture of the liquid and water begins to boil, because the vapour pressure of the mixture becomes equal to the atmospheric pressure.

Obviously, this happens at a temperature that is lower than the boiling point of the substance or that of water. Thus, an organic compound boils below its boiling points and chances of decomposition avoided. For example, a mixture of aniline (b.p 453 K) with decomposition and water (b.p. 373 K) under normal atmospheric pressure boils at 371K. At this temperature the

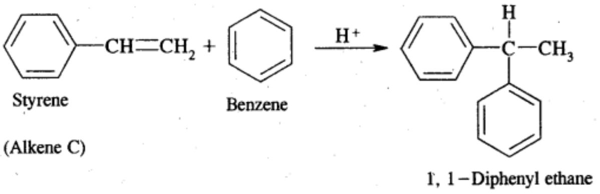


Steam Distillation water boils at 371 K. At this temperature, the vapour pressure of water is 717 mm and that of aniline is 43 mm and therefore the total pressure is equal, to 760 mm. Thus, in steam distillation, the liquid gets distilled at a temperature lower than its boiling point and chances of decomposition avoided. The proportion of water and liquid in the mixture that distils over is given by the relation.

$$\frac{\omega_1}{\omega_2} = \frac{P_1 \times 18}{P_2 \times M}$$

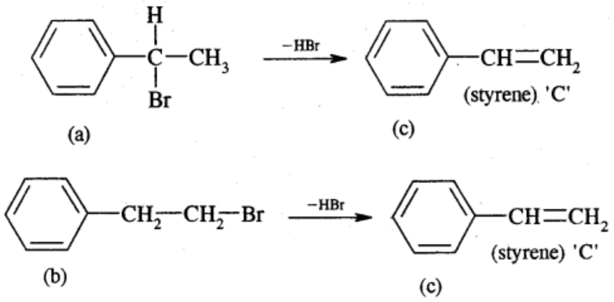
where w_1 and w_2 stand for the masses of water and liquid that distils over. P_1 and P_2 are vapour pressure of water and of liquid at the distillation temperature and M is the molecular mass of the liquid.

2. **Ans:** Alkene (C) on reaction with benzene in the presence of H+ ions give 1, 1-Diphenyl ethane. Therefore, C must be styrene as depicted below

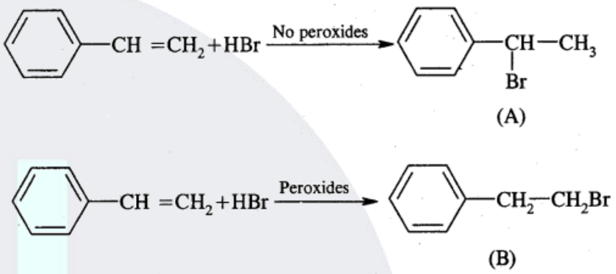


Now dehydrobromination of A and B give the same alkene C, i.e., styrene.

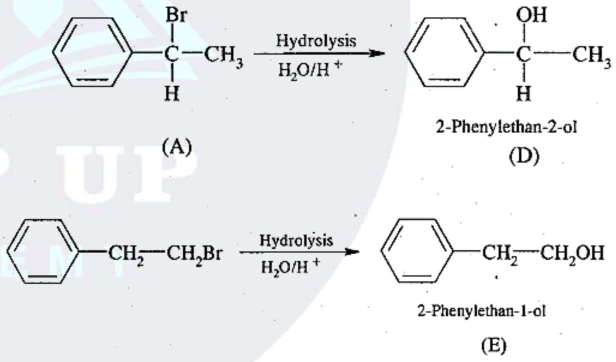
∴ A and B must be isomeric alkyl bromide



A and B can be obtained by the addition of HBr in the presence and absence of peroxide to styrene.



Hydrolysis of A and B give isomeric alcohols (D) & (E) as



3. **Ans:** The species which are generated as a result of bond fission are called reaction intermediates. The important reaction intermediates are:

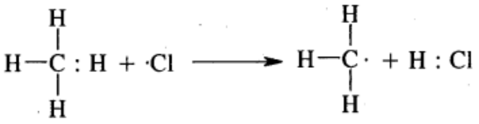
   1. Free Radicals: A free radical may be defined as an atom or group of atoms having an impaired electron. These are obtained as a result of homolytic fission of covalent bonds.

$$A:B \xrightarrow{\text{Homolytical Fission}} \underset{(\text{Free radicals})}{A' + B'}$$

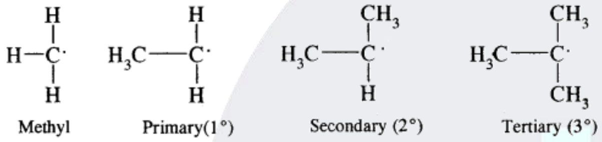
These free radicals are neutral particles, extremely transient, (short-lived) and highly reactive. They get consumed as soon as they are formed. They pair up their electron with another electron from wherever it is available. They occur only as a reaction intermediate. Their presence is felt in reactions, but cannot be isolated in a free state. For example, dissociation of Cl2 gas in the presence of Ultraviolet light produces free radicals.

$$Cl:Cl \xrightarrow{UV\ light} \underset{(Free\ radicals)}{\cdot Cl + \cdot Cl}$$

The alkyl free radicals are obtained when free radical: Cl reacts with alkanes.

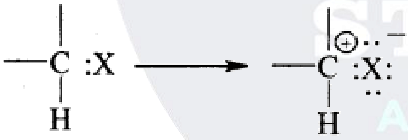


Free radical may be primary, secondary, tertiary depending upon whether, one, two or three carbon atom attached to the carbon atoms carrying the odd electron.



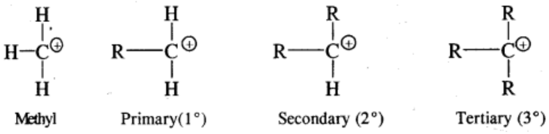
The stability is $CH_3 < 1° < 2° < 3°$.

2. Carbocation or carbonium ion: It is defined as a group of atoms that contain positively charged carbon having only six electrons. It is obtained by heterolytic fission of a covalent bond involving a carbon atom.



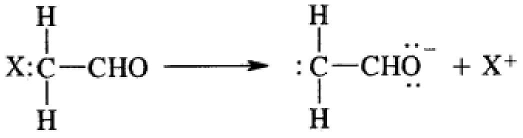
Carbocation

They are also classified as primary, secondary and tertiary depending upon whether one, two or three carbon atoms are attached to the carbon bearing the positive charge as:



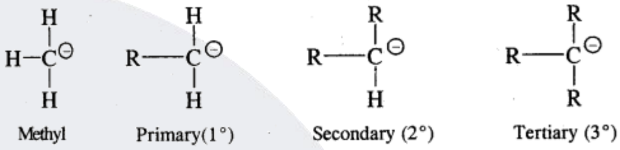
Thus, the order of stability if $CH_3^+ < 1° < 2° < 3°$.

3. Carbanion: A carbanion may be defined as a species containing a carbon atom carrying a negative charge. These are generated by the atom in which the atom linked to carbon goes without the bonding electrons. As a result of this carbon acquires a negative charge. For example, the removal of hydrogen of methyl part of acetaldehyde molecule as H+ ion leaving both the electron on carbon.



Carbanion

They are also very reactive species. They are also classified as primary, secondary and tertiary depending upon whether one, two or three carbon atoms are attached to the carbon atom bearing negative charge.



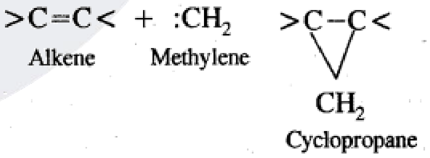
The order of stability is the reverse of free radicals and carbocations

$CH_3^- > 1° > 2° > 3°$.

(iv) Carbenes: The carbenes are reactive neutral species in which carbon atom has six electrons in the valency shell out of which two are shared. The simplest carbene is methylene (CH_2). It is formed when diazomethane is decomposed by the action of light.

$$\underset{Diazomethane}{CH_2N_2} \xrightarrow{light} \underset{Methylene\ carbene}{:CH_2 + N_2}$$

It is very reactive. It reacts with alkenes by adding to the double bond forming cyclopropane.



4. **Ans:** Mass of $BaSO_4$ = 0.582 g

$BaSO_4 = S$

233 = 32

233g of $BaSO_4$ contain sulphur = 32g

582 g of $BaSO_4$ contains sulphur

$$= \frac{32 \times 0.582}{233}$$

$$\text{Percentage of sulphur} = \frac{\text{Wt. of sulphur}}{\text{Wt. of compound}} \times 100$$

$$= \frac{32 \times 0.582}{233 \times 0.395} \times 100$$

$= 20.24\%$

5. **Ans:** Mass of AgBr formed = 0.12g

188 g of AgBr contains bromine = 80g.

Therefore, 0.12g of AgBr will contain bromine

$$= \frac{80 \times 0.12}{188} = 0.051 \text{ g}$$

Percentage of bromine $= \frac{0.051}{0.15} \times 100 = 34\%$

Assertion Reason Answer:

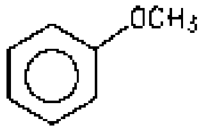
1. (i) Both A and R are correct and R is the correct explanation of A.
2. (iv) A is not correct but R is correct.

Case Study Answer:

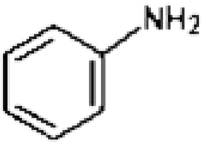
1. **Answer:**

(1) (b) $CH_3CH_2CH_2 — NO_2$

(2)



(3)



(4) (a) Inductive effect

2. **Answer:**

(1) (a) C > B > A

(2) (a) $CH_3\dot{C}H_2$ and $\dot{C}l$

(3) (b) trigonal planar

(4) (b) II > I > IV > III

◆ ◆

Hydrocarbons 13

Introduction

The term ‘hydrocarbon’ is self-explanatory meaning compounds of carbon and hydrogen only. Hydrocarbons hold economic potential in our daily life. Natural gas and petroleum are chief sources of aliphatic hydrocarbons at the present time, and coal is one of the major sources of aromatic hydrocarbons. Petroleum is a dark, viscous mixture of many organic compounds, most of them being hydrocarbons, mainly alkanes, cycloalkanes and aromatic hydrocarbons.

Classification

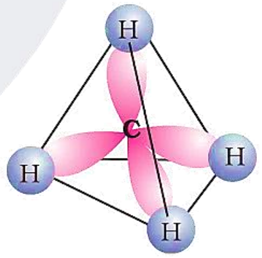
As we are quite aware that there are different types of hydrocarbons. Depending upon the types of carbon-carbon bonds present, they can be classified into three main categories:

1. Saturated hydrocarbons.
2. Unsaturated hydrocarbons.
3. Aromatic hydrocarbons.

Saturated hydrocarbons contain carbon-carbon and carbon-hydrogen single bonds. If different carbon atoms are joined together to form open chain of carbon atoms with single bonds, they are termed as alkanes. On the other hand, if carbon atoms form a closed chain or ring, they are termed as cycloalkanes. Unsaturated hydrocarbons contain carbon-carbon multiple bonds – double bonds, triple bonds or both. Aromatic hydrocarbons are a special type of cyclic compounds.

Alkanes

These are the saturated chains of hydrocarbons containing carbon-carbon single bonds. Methane (CH_4) is the first member of this family containing single carbon atom. Since it is found in coal mines and marshy areas, is also known as ‘marsh gas’. These hydrocarbons exhibited low reactivity or no reactivity under normal conditions with acids, bases and other reagents, they were earlier known as paraffins. The general formula for alkane is C_nH_{2n+2}, where n stands for number of hydrogen atoms in the molecule.



Structure of Methane

1. Nomenclature

For nomenclature of alkanes in IUPAC system, the longest chain of carbon atoms containing the single bond is selected. Numbering of the chain is done from the one end so that maximum carbon will be included in chain. The suffix ‘ane’ is used for alkanes. The first member of the alkane series is CH_4 known as methylene (common name) or methene (IUPAC name). IUPAC names of a few members of alkenes are given below:

S. No.	Structure	IUPAC Name
1.	CH_4	Methane
2.	C_2H_6	Ethane
3.	C_3H_8	Propane

4.	C_4H_{10}	Butane
5.	C_5H_{12}	Pentane
6.	C_6H_{14}	Hexane
7.	C_7H_{16}	Heptane
8.	C_8H_{18}	Octane
9.	C_9H_{20}	Nonane
10.	$C_{10}H_{22}$	Decane

2. Preparation of Alkanes

Though petroleum and natural gas are the main sources of alkanes, it can be prepared by several other methods as well.

i. From unsaturated hydrocarbons: The addition of dihydrogen to unsaturated hydrocarbons like alkenes and alkynes in the presence of a suitable catalyst under a given set of conditions produces saturated hydrocarbons or alkanes. This process of addition of dihydrogen is known as hydrogenation process.

$$CH_2{=}CH_2 + H_2 \longrightarrow CH_3\text{-}CH_3$$

$$CH{\equiv}CH + 2H_2 \longrightarrow CH_3\text{-}CH_3$$

ii. From alkyl halides

a) **Reduction:** Alkyl halides undergo reduction with zinc and dilute hydrochloric acid to give alkanes. In general, the reaction can be represented as

$$CH_3\text{-}Cl \longrightarrow CH_4$$

b) **Wurtz reaction:** Alkyl halides on treatment with sodium metal in dry ether give higher alkanes. This reaction is known as Wurtz reaction.

$$CH_3Br + 2Na + BrCH_3 \longrightarrow CH_3\text{-}CH_3 + 2NaBr$$

iii. From carboxylic acids

a) **By decarboxylation of carboxylic acids:** Sodium salts of carboxylic acids on heating with soda lime give alkanes containing one carbon atom less than the carboxylic acid. A molecule of carbon dioxide is eliminated which dissolves in NaOH to form sodium carbonate.

$$CH_3COONa + NaOH \longrightarrow CH_4 + Na_2CO_3$$

b) **Kolbe's electrolytic method:** An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms at anode.

$$CH_3COONa + 2H_2O \longrightarrow CH_3\text{-}CH_3 + 2CO_2 + H_2 + NaOH$$

3. Properties of Alkanes

I. Physical Properties

i. **State:** Due to the weak van der Waals forces, the first four members C1 to C4 i.e., methane, ethane, propane and butane are gases. From C5 to C17 are liquids and those containing 18 carbon atoms or more are solids at 298 K. They all are colourless and odourless.

ii. **Solubility:** Alkanes are generally insoluble in water or in polar solvents, but they are soluble in non-polar solvents like, ether, benzene, carbontetrachloride etc. The solubility of alkanes follows the property "Like Dissolves like".

iii. **Boiling point:** The boiling points of straight chain alkanes increase regularly with the increase of number of carbon atoms. This is due to the fact that the intermolecular van der Waals forces increase with increase in the molecular size or the surface area of the molecule.

II. **Chemical Properties**

Generally, alkanes show inertness or low reactivity towards acids, bases, oxidizing and reducing agents at ordinary conditions because of their non-polar nature and absence of π bond. The C–C and C–H bonds are strong sigma bonds which do not break under ordinary conditions but they undergo certain reactions under given suitable conditions.

i. **Halogenation reaction:** When hydrogen atom of an alkane is replaced by a halogen, it is known as halogenation reaction. Halogenation takes place either at high temperature (300–500°C) or in the presence of diffused sunlight or ultraviolet light.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

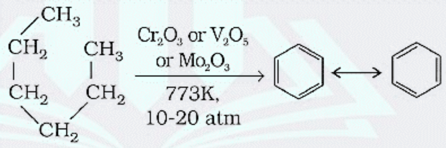
ii. **Combustion:** Alkanes on heating in presence of air gets completely oxidized to carbon dioxide and water. It burns with a non-luminous flame. The combustion of alkanes is an exothermic process i.e., it produces a large amount of heat.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

iii. **Controlled oxidation:** When methane and dioxygen compressed at 100 atm are passed through heated copper tube at 523K yield methanol.

$$2CH_4 + O_2 \longrightarrow 2CH_3OH$$

iv. **Aromatization:** The conversion of aliphatic compounds into aromatic compounds is known as aromatisation. n-Alkanes having six or more carbon atoms on heating to 773K at 10–20 atmospheric pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina get dehydrogenated and cyclised to benzene and its homologues. This reaction is also known as reforming.



v. **Reaction with steam:** Methane reacts with steam at 1273K in the presence of nickel catalyst to form carbon monoxide and dihydrogen. This method is used for industrial preparation of dihydrogen gas.

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

Alkenes

Alkenes are unsaturated hydrocarbons containing at least one carbon-carbon double bond with general formula C_nH_{2n}. Alkenes are also known as olefins (oil forming) since the first member, ethylene or ethene (C_2H_4) was found to form an oily liquid on reaction with chlorine.

1. Nomenclature

For nomenclature of alkenes in IUPAC system, the longest chain of carbon atoms containing the double bond is selected. Numbering of the chain is done from the end which is nearer to the double bond. The suffix 'ene' replaces 'ane' of alkanes. The first member of the alkene series is C_2H_4 known as ethylene (common name) or ethene (IUPAC name). IUPAC names of a few members of alkenes are given below:

S.No.	Structure	IUPAC Name
1.	C_2H_4	Ethene
2.	C_3H_6	Propene
3.	C_4H_8	Butene
4.	C_5H_{10}	Pentene
5.	C_6H_{12}	Hexene

6.	C_7H_{14}	Heptene
7.	C_8H_{16}	Octene
8.	C_9H_{18}	Nonene
9.	$C_{10}H_{20}$	Dekene

2. Preparation

i. **From alkynes:** Alkynes undergo partial reduction with calculated amount of dihydrogen producing alkenes.

$$CH\equiv CH + H_2 \longrightarrow CH_2=CH_2$$

ii. **From alkyl halides:** Alkyl halides (R–X) on heating with alcoholic potash eliminates one molecule of halogen acid to form alkenes. This reaction is known as dehydrohalogenation i.e., removal of halogen acid.

$$CH_3CH_2Cl \longrightarrow CH_2=CH_2 + HCl$$

iii. **From alcohols by acidic dehydration:** Alcohols on heating with concentrated sulphuric acid form alkenes with the elimination of one water molecule since a water molecule is eliminated from the alcohol molecule in the presence of an acid, this reaction is known as acidic dehydration of alcohols.

$$CH_3CH_2OH \longrightarrow CH_2=CH_2 + H_2O$$

3. Properties of Alkenes

I. Physical properties

i. The first three members of alkenes are gases, the next fourteen are liquids and the higher ones are solids.

ii. Ethene is a colourless gas with a faint sweet smell. All other alkenes are colourless and odourless, insoluble in water but fairly soluble in non-polar solvents like benzene, petroleum ether.

iii. They show a regular increase in boiling point with increase in size i.e., every —CH_2 group added increase the boiling point by 20–30K.

II. Chemical properties

i. **Addition of dihydrogen:** Alkenes adds one mole of dihydrogen gas in presence of catalysts such as Ni at 200–250°C, or finely divided Pt or Pd at room temperature to give an alkane.

$$CH_2=CH_2 + H\text{-}H \longrightarrow CH_3\text{-}CH_3$$

ii. **Addition of halogens:** Halogens like bromine or chlorine add up to alkene to form vicinal dihalides in presence of CCl_4 as solvent. The order of reactivity of halogens is F > Cl > Br > I.

$$CH_2=CH_2 + Br\text{-}Br \longrightarrow Br\text{-}CH_2\text{-}CH_2\text{-}Br$$

iii. **Addition of hydrogen halides:** Hydrogen halides (HCl, HBr, HI) add upto alkenes to form alkyl halides. The order of reactivity of hydrogen halides is HI > HBr > HCl. Like addition of halogens to alkenes, addition of hydrogen halides is an example of electrophilic addition reaction.

$$CH_2=CH_2 + H\text{–}Br \longrightarrow CH_3\text{–}CH_2\text{–}Br$$

Markovnikov rule: According to the rule, the negative part of the addendum (adding molecule) adds to that carbon atom of the unsymmetrical alkene which is maximum substituted or which possesses lesser number of hydrogen atoms.

$$CH_3CH=CH_2 + HBr \longrightarrow CH_3\text{—}CH(Br)\text{—}CH_3$$

Anti Markovnikov addition or Peroxide effect or Kharash effect: In the presence of peroxide, addition of HBr to unsymmetrical alkenes like propene takes place contrary to the Markovnikov rule. This happens only with HBr but not with HCl or HI. This reaction is known as peroxide or Kharash effect or addition reaction anti to Markovnikov rule.

$$CH_3CH=CH_2 + HBr \longrightarrow CH_3\text{–}CH_2\text{–}CH_2\text{–}Br$$

iv. **Polymerisation:** Polymerisation is the process where monomers combines together to form polymers. The large molecules thus obtained are called polymers. Other alkenes also undergo polymerisation.

$$n(CH_2{=}CH_2) \longrightarrow (-CH_2-CH_2-)_n$$

Alkenes

Like alkenes, alkynes are also unsaturated hydrocarbons with general formula C_nH_{2n-2}. They contain at least one triple bond between two carbon atoms. These have four H-atoms less compared to alkanes. The first stable member of alkyne series is ethyne commonly known as acetylenes.

1. Nomenclature

In common system, alkynes are named as derivatives of acetylene. In IUPAC system, they are named as derivatives of the corresponding alkanes replacing 'ane' by the suffix 'yne'. The position of the triple bond is indicated by the first triply bonded carbon. Common and IUPAC names of a few members of alkyne series are given in the table below:

S.No.	Structure	IUPAC Name
1.	C_2H_2	Ethyne
2.	C_3H_4	Propyne
3.	C_4H_6	Butyne
4.	C_5H_8	Pentyne
5.	C_6H_{10}	Hexyne

2. Preparation

i. **From calcium carbide:** On industrial scale, ethyne is prepared by reacting calcium carbide with water. Calcium carbide is prepared by heating quick lime with coke. Quick lime can be obtained by heating limestone as shown in the following reactions:

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + 3C \longrightarrow CaC_2 + CO$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

ii. **From vicinal dihalides**: Vicinal dihalides on treatment with alcoholic potassium hydroxide undergo dehydrohalogenation. One molecule of hydrogen halide is eliminated to form alkenyl halide which on treatment with sodamide gives alkyne.

$$CH_2(Br)-CH_2(Br) + KOH \longrightarrow CH_2{=}CH_2 \longrightarrow CH{\equiv}CH$$

4. Properties of Alkenes

I. Physical properties

i. The first three members (acetylene, propyne and butynes) are gases, the next eight are liquids and higher ones are solids.

ii. All alkynes are colourless. All alkynes except ethyne which have an offensive characteristic odour, are odourless.

iii. Alkynes are weakly polar in nature and nearly insoluble in water. They are quite soluble in organic solvents like ethers, carbon tetrachloride and benzene.

iv. Their melting point, boiling point and density increase with increase in molar mass.

II. **Chemical properties**

i. **Addition of dihydrogen:** Alkynes contain a triple bond, so they add up, two molecules of dihydrogen.

$$CH\equiv CH + H_2 \longrightarrow CH_2{=}CH_2 \longrightarrow CH_3\text{-}CH_3$$

ii. Addition of halogens: Alkynes contain a triple bond, so they add up, two molecules of halogen.

$$CH\equiv CH + Cl_2 \longrightarrow CH(Cl){=}CH(Cl) \longrightarrow CH(Cl)_2\text{-}CH(Cl)_2$$

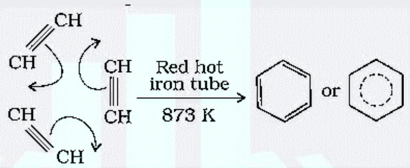
iii. **Addition of hydrogen halides:** Two molecules of hydrogen halides (HCl, HBr, HI) add to alkynes to form gem dihalides (in which two halogens are attached to the same carbon atom).

$$CH\equiv CH + HCl \longrightarrow CH_2{=}CH(Cl)$$

iv. **Addition of water:** Like alkanes and alkenes, alkynes are also immiscible and do not react with water. However, one molecule of water adds to alkynes on warming with mercuric sulphate and dilute sulphuric acid at 333K to form carbonyl compounds.

$$CH\equiv CH + H_2O \longrightarrow CH_3\text{-}CHO$$

v. **Polymerisation:** Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerization. Three molecules polymerise to form benzene, which is the starting molecule for the preparation of derivatives of benzene, dyes, drugs and large number of organic compounds.



vi. **Oxidation:**

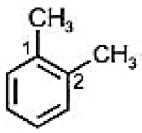
$$2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O$$

Aromatic Hydrocarbon

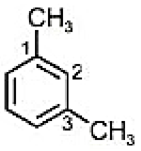
Aromatic hydrocarbons are also known as 'arenes'. Since most of them possess pleasant odour (Greek; aroma meaning pleasant smelling), the class of compounds are known as 'aromatic compounds'. Most of the compounds are found to have benzene ring. Benzene ring is highly unsaturated and in a majority of reactions of aromatic compounds, the unsaturation of benzene ring is retained. Aromatic compounds containing benzene ring are known as benzenoids and those, not containing a benzene ring are known as non-benzenoids.

1. Nomenclature

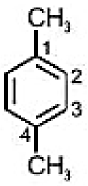
Since all the six hydrogen atoms in benzene are equivalent; so, it forms one and only one type of monosubstituted product. When two hydrogen atoms in benzene are replaced by two similar or different monovalent atoms or groups, three different position isomers are possible which differ in the position of substituents. So, we can say that disubstituted products of benzene show position isomerism. The three isomers obtained are 1, 2 or 1, 6 which is known as the ortho (o-), the 1, 3 or 1, 5 as meta (m-) and 1, 4 as para (p-) disubstituted compounds.



1, 2-Dimethyl benzene
or o-Dimethylbenzene or o-Xylene



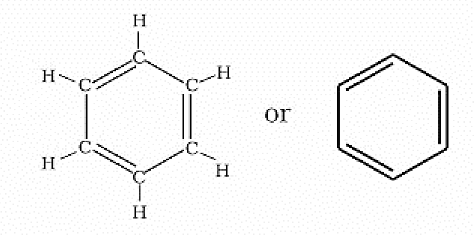
1, 3-Dimethylbenzene
or m-Dimethylbenzene or m-Xylene



1, 4-Dimethyl benzene
or p-Dimethylbenzene or p-Xylene

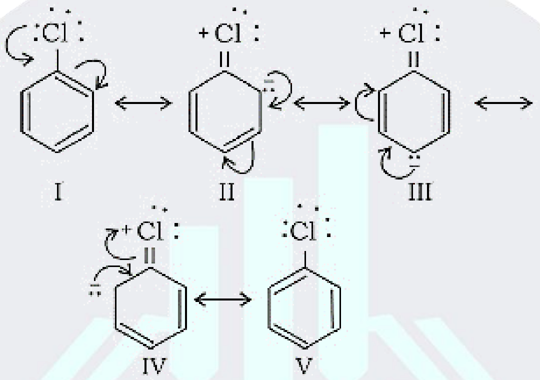
2. Structure

The molecular formula of benzene, C_6H_6, indicates a high degree of unsaturation. All the six carbon and six hydrogen atoms of benzene are identical. On the basis of this observation August Kekule in 1865 proposed the following structure for benzene having cyclic arrangement of six carbon atoms:



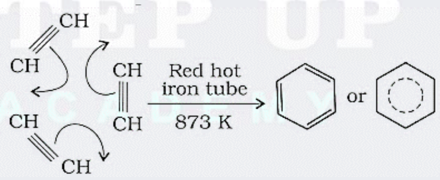
3. Resonance

Even though the double bonds keep on changing their positions. The structures produced is such that the position of nucleus remains the same in each of the structure. The structural formula of such a compound is somewhat intermediate (hybrid) between the various propose formulae. This state is known as Resonance.

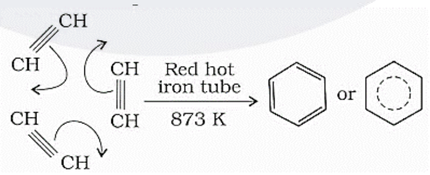


4. Preparation of Benzene

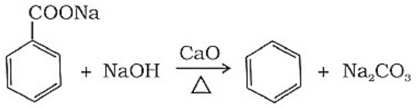
i. **Cyclic polymerisation of ethyne:** Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerization.



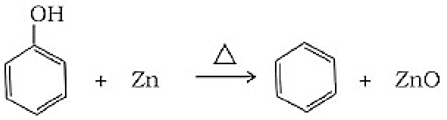
ii. **Decarboxylation of aromatic acids:** Sodium salt of benzoic acid i.e., sodium benzoate on heating with sodalime gives benzene.



iii. **Decarboxylation of aromatic acids:** Sodium salt of benzoic acid i.e., sodium benzoate on heating with sodalime gives benzene.



iv. **Reduction of phenol:** Phenol is reduced to benzene by passing its vapour over heated zinc dust.



5. Properties of Benzene

I. Physical Properties

i. Aromatic hydrocarbons are non-polar molecules and are usually colourless liquids or solids with a characteristic aroma.

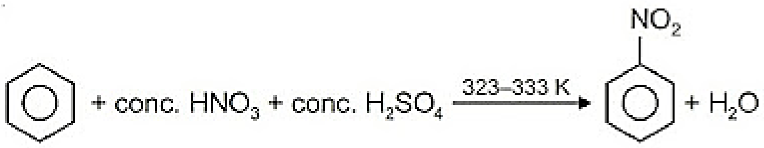
ii. The napthalene balls used in toilets and for preservation of clothes because of unique smell of the compound.

iii. Aromatic compounds are insoluble in water but soluble in organic solvents such as alcohol and ether.

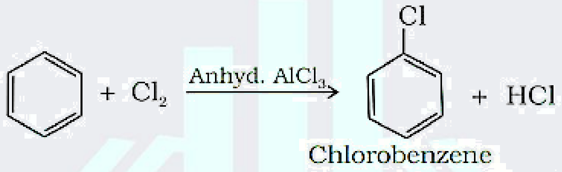
iv. They burn with sooty flame.

II. Chemical properties

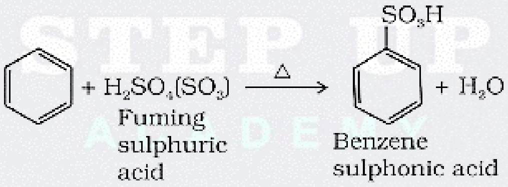
i. **Nitration:** A nitro group is introduced into the benzene ring when benzene is heated with a mixture of concentrated nitric acid and concentrated sulphuric acid.



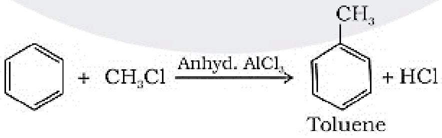
ii. **Halogenation:** Arenes undergo halogenation when it is treated with halogens in presence of Lewis catalyst such as anhy. $FeCl_3$, $FeBr_3$ or $AlCl_3$ to yield haloarenes.



iii. **Sulphonation**: The replacement of a hydrogen atom by a sulphonic acid group in a ring is called sulphonation. It is carried out by heating benzene with fuming sulphuric acid or oleum (conc. H_2SO_4 + SO_3).



iv. **Friedel-Crafts alkylation reaction:** When benzene is treated with an alkyl halide in the presence of anhydrous aluminium chloride, alkylbenzene is formed.



Activating Groups: Electron donating groups (EDG, +M, +I, +H. C. effect) in the benzene ring will more stabilize the σ-complex (Arenium ion complex) with respect to that of benzene and hence they are known as activator.

Deactivating Groups: Electron drawing groups (–M, –I effects) will destabilize σ-complex as compared to that of benzene. Therefore, substituted benzenes where substituents are electron withdrawing decreases reactivity towards SE reactions.

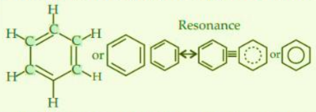
Summary-

1. **Hydrocarbons:** The compounds which are made up of only carbon and hydrogen elements.
2. LPG (Liquefied petroleum gas), LNG (Liquefied natural gas) and CNG (Compressed natural gas) are important fuels.

3. Alkanes are saturated hydrocarbons having general formula C_nH_{2n+2}. They contain only C—C and C—H sigma bonds.
4. Alkenes are unsaturated hydrocarbons having general formula C_nH_{2n}. They contain a carbon-carbon double bond.
5. Alkynes are unsaturated hydrocarbons having general formula C_nH_{2n-2}. They contain a carbon-carbon triple bond.
6. Alkanes exhibit conformational isomerism due to almost free rotation about C—C sigma bond.
7. Alkenes exhibit geometric isomerism due to restricted rotation about carbon-carbon double bond.
8. The cis isomer is more polar and has higher boiling point than the trans isomer. On the other hand the melting point of trans isomer is higher.
9. **Cracking:** The process of decomposing higher hydrocarbons into lower hydrocarbons by strong heating.
10. **Reforming or Aromatisation:** The process of converting aliphatic and alicyclic hydrocarbons into aromatic hydrocarbons by heating in the presence of suitable catalysts such as platinum.
11. **Grignard reagent:** RMgX, Alkyl magnesium halide.
12. Soda-lime decarboxylation of sodium salts of carboxylic acids leads to formation of alkane with one carbon less than the starting compound.
13. Dehydrohalogenation of Alkyl halides is carried out by heating with alcoholic solution of KOH.
14. Branched chain hydrocarbons have lower boiling points than straight chain hydrocarbons having same number of carbon atoms.
15. Among isomeric xylenes, para isomer has the highest melting point.
16. **Baeyer's reagent:** 1% cold and alkaline solution of $KMnO_4$.
17. **Markovnikov's rule:** During electrophilic addition across unsymmetrical double bond, the negative part of the adding molecule goes to that carbon which has a smaller number of hydrogen atoms.
18. **Kharash effect:** Anti-Markovnikov addition of HBr to alkenes in the presence of organic peroxides.
19. Arenes are aromatic hydrocarbons. They contain at least one benzene ring.
20. The important reactions of alkanes are free radical substitution reactions while that of alkenes and alkynes are electrophilic addition reactions.
21. Aromatic hydrocarbons are undergoing mainly electrophilic substitution reactions inspire of high degree of unsaturation present in them.
22. Aromaticity in aromatic compounds is due to the presence cyclic, delocalized system of $(4n+2)\ \pi$ electrons.
23. Substitution reactions are common for alkanes and arenes whereas addition reactions are common for alkenes and alkynes.
24. The catalyst for Friedel-Craft reaction is anhydrous $AlCl_3$.
25. Terminal alkynes are acidic in character.
26. Electron releasing groups increase the reactivity of benzene ring towards electrophilic substitution reactions. Some examples are —R, —OH, $—NH_2$, —OR, $—NHCOCH_3$, etc.

Class : 11th Chemistry
Chapter- 13: Hydrocarbons

- Types: Benzenoids – contain benzene ring, Non-benzenoids – does not contain benzene ring.
- Isomerism: Ortho (o-), Meta (m-), Para (p-) Resonance and
- Structure:



- Aromaticity: Planarity, complete delocalisation of the TT–electros in the ring, presence of (4n + 2) π electrons in the ring where n is an integer (n = 0,1,2,......) (Huckel rule)

Preparation:

- Cyclic polymerisation of ethyne

$C_6H_5COONa + NaOH \xrightarrow[\Delta]{CaO} C_6H_6 + Na_2CO_3$

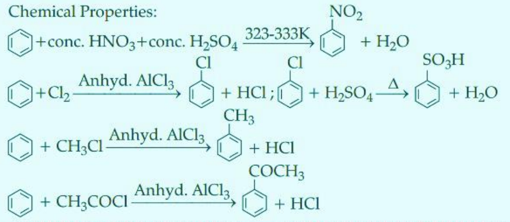
$C_6H_5OH + Zn \xrightarrow{\Delta} C_6H_6 + ZnO$

Aromatic Hydrocarbon

Physical Properties:

- Non-polar, usually colourless liquids or solids with characteristic aroma.
- Immiscible with water but miscible with organic solvents.
- Burns with sooty flame.

Chemical Properties:



Compounds of Carbon and Hydrogen

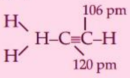
Classification
-Saturated: Contain C-C and C-H single bonds. (alkanes)
-Unsaturated: Contain C-C multiple bonds.
-Aromatic: Contain Cyclic Compounds

Mechanism of Electrophilic substitution reactions
(i). Generation of Electrophile
(ii). Formation of carbocation intermediate
(iii). Removal of proton

Hydrocarbons

Alkenes(C_nH_{2n-2})

- IUPAC name: replacing 'ane' by the suffix 'yne'.
- Shows position and chain isomerism



Preparation:

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

$CaO + 3C \longrightarrow CaC_2 + CO$

$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

$CH_2Br-CH_2Br + KOH \xrightarrow[-KBr,\ -H_2O]{alcohol} H_2C=CHBr \xrightarrow[-NaBr,\ -NH_3]{NaNH_2} CH\equiv CH$

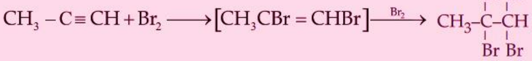
Physical Properties:

- First three members are gases, next eight are liquids and higher ones are solids.
- Colourless, ethyne has characteristic odour and other are odourless.
- Lighter than water, immiscible with water but soluble in organic solvents.
- m.p, b.p. and density increase with increase in molar mass.

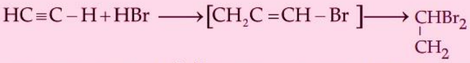
Chemical Properties:

$HC\equiv CH + Na \longrightarrow HC\equiv CNa + 1/2\,H_2$

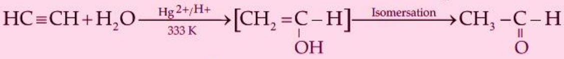
$HC\equiv CH + H_2 \xrightarrow{Pt/Pd/Ni} [H_2C=CH_2] \xrightarrow{H_2} CH_3-CH_3$



$CH_3-C\equiv CH + Br_2 \longrightarrow [CH_3CBr=CHBr] \xrightarrow{Br_2} CH_3-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}H$

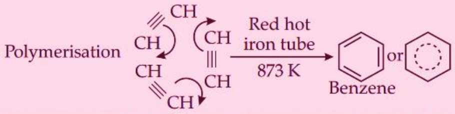


$HC\equiv C-H + HBr \longrightarrow [CH_2C=CH-Br] \longrightarrow \underset{CH_2}{CHBr_2}$

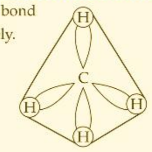


$HC\equiv CH + H_2O \xrightarrow[333\,K]{Hg^{2+}/H^+} [CH_2=\underset{OH}{C}-H] \xrightarrow{Isomersation} CH_3-\underset{O}{\overset{}{C}}-H$

Polymerisation



- H-C-H bond angles – 190.5, C-C and C-H bond lengths are 154 pm and 112 pm respectively.
- Shows structural and chain isomerism.



Preparation :

$CH_2=CH_2 + H_2 \xrightarrow{pt/pd/Ni} CH_3-CH_3$

$Ch_3Cl + H_2 \xrightarrow{zn,H^+} CH_4 + HCl$

Wurtz reaction :

$CH_3Br + 2Na + BrCH_3 \xrightarrow{Dryether} CH_3-CH_3 + 2NaBr$

$CH_3COO^-Na^+ + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$

$2CH_3COONa + 2H_2O \longrightarrow C_2H_6 + 2CO_2 + H_2 + 2NaOH$

- Physical Properties:

Non-polar, weak van der Waals forces, colourless, odourless.

B.P. increases with increases in molecular size.

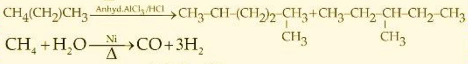
Chemical Properties:

$CH_4 \xrightarrow[hv/-HCl]{+Cl_2} CH_3Cl + \xrightarrow[hv/-HCl]{+Cl_2} CH_2Cl_2 \xrightarrow[hv/-HCl]{+Cl_2} CHCl_3 \xrightarrow[hv/-HCl]{+Cl_2}$

$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$

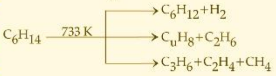
$2CH_4 + O_2 \xrightarrow{Cu/523K/100atm} 2CH_3OH$

$CH_4 + O_2 \xrightarrow[\Delta]{Mn_2O_3} HCHO + H_2O$

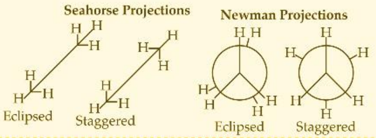


$CH_4(CH_2)CH_3 \xrightarrow{Anhyd.AlCl_3/HCl} CH_3-CH-(CH_2)_2-\underset{CH_3}{C}H_3 + CH_3-CH_2-\underset{CH_3}{C}H-CH_2-CH_3$

$CH_4 + H_2O \xrightarrow[\Delta]{Ni} CO + 3H_2$



$C_6H_{14} \xrightarrow{733\,K} C_6H_{12} + H_2;\ C_uH_8 + C_2H_6;\ C_3H_6 + C_2H_4 + CH_4$

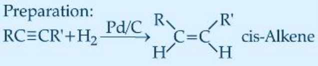


Alkene(C_2H_{2n-2})

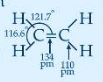
Alkenes(C_2H_{2n})

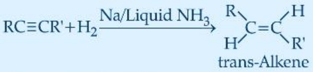
- Shows structural and geometrical isomerism

Preparation:



$RC\equiv CR' + H_2 \xrightarrow{Pd/C}$ cis-Alkene





$RC\equiv CR' + H_2 \xrightarrow{Na/Liquid\ NH_3}$

trans-Alkene

$H_3C-CH_2X \xrightarrow[\Delta]{Alc.KOH} H_2C=CH_2$

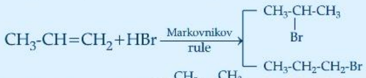
$CH_2Br-CH_2Br + Zn \longrightarrow CH_2=CH_2 + ZnBr_2$

$H_3CCH_2OH \xrightarrow[\Delta]{conc.H_2SO_4} CH_2=CH_2 + H_2O$

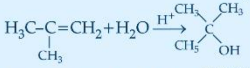
- Physical Properties :
  - Ethene is a colourless gas with faint sweet smell.
  - All other are colourless and odourless, insoluble in water but fairly soluble in non-polar solvents.
  - Increase in b.p. with increased molecular size.
- Chemical Properties:

$CH_2=CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2-CH_2Br$

$CH_2=CH_2 + HBr \longrightarrow CH_3CH_2Br$



$CH_3\text{-}CH=CH_2 + HBr \xrightarrow[rule]{Markovnikov} CH_3\text{-}\underset{Br}{C}H\text{-}CH_3;\ CH_3\text{-}CH_2\text{-}CH_2\text{-}Br$



$H_3C-\underset{CH_3}{C}=CH_2 + H_2O \xrightarrow{H^+}$

$CH_3-CH=CH-CH_3 \xrightarrow{KMnO4/H^+} 2CH_3COOH$

$n(CH_2=CH_2) \xrightarrow[Catalyst]{HighTemp/Pressure} -(CH_2-CH_2)_{\overline{n}}$

$n(CH_3-CH=CH_2) \xrightarrow[Catalyst]{HighTemp/Pressure} -(CH-CH_2)_{\overline{n}}$

Important Questions

Multiple Choice questions-

1. Which of the following compounds will exhibit geometrical isomerism?
   (a) 1 – Phenyl – 2 – butene
   (b) 3 – Phenyl – 1 – butene
   (c) 2 – Phenyl – 1 butene
   (d) 1, 1 – Diphenyl – propene.
2. Hydrocarbon containing following bond is most reactive
   (a) C ≡ C
   (b) C = C
   (c) C – C
   (d) All of these
3. A gas decolourised by KMno4 solution but gives no precipitate with ammoniacal cuprous chloride is
   (a) Ethene
   (b) Propane
   (c) Propene
   (d) Methane
4. A dibromo derivative of an alkane reacts with sodium metal to form an alicyclic hydrocarbon. The derivative is ______
   (a) 1, 4-dibromobutane
   (b) 1, 2-dibromoethane
   (c) Carbon
   (d) None of the above
5. Reaction of HBr with propene in the presence of peroxide gives:
   (a) 3 – Bromo propane
   (b) Allyl bromide
   (c) n – Propyl bromide
   (d) Isoproyl bromide
6. Which branched chain isomer of the hydrocarbon with molecular mass 72u gives only one isomer of mono substituted alkyl halide?
   (a) Neopentane
   (b) Carbon
   (c) Isohexane
   (d) Neohexane
7. Aromatic compounds burn with a sooty flame because?
   (a) They have a ring structure of carbon atoms
   (b) They have a relatively high percentage of hydrogen
   (c) They have a relatively high percentage of carbon
   (d) They resist reaction with oxygen of air
8. The lowest alkene, that is capable of exhibiting geometrical isomerism is
   (a) Ethene
   (b) But – 1- ene
   (c) But – 2 – ene
   (d) Propene
9. Which one of these is NOT TRUE for benzene?
   (a) Heat of hydrogenation of benzene is less than the theoretical value
   (b) There are three carbon-carbon single bonds and three carbon-carbon double bonds
   (c) It forms only one type of monosubstituted product
   (d) The bond angle between carbon-carbon bonds is 120o
10. Ethyl benzene cannot be prepared by ____.
    (a) Wurtz Reaction
    (b) Wurtz Fittig reaction
    (c) Clemmensen Reduction
    (d) Carbon
11. Propyne on polymerization yields
    (a) Mesitylene
    (b) Benzene
    (c) Ethyl benzene
    (d) Propyl benzene.
12. A gas decolourised by $KMnO_4$ solution but gives no precipitate with ammoniacal cuprous chloride is
    (a) Ethene
    (b) Propane
    (c) Propene
    (d) Methane

13. Among the following compounds the one that is most reactive towards electrophilic nitration is
    (a) Toluene
    (b) Benzene
    (c) Benzoic Acid
    (d) Nitrobenzene
14. HBr reacts with $CH_2 = CH - OCH_3$ under anhydrous conditions at room temperature to give
    (a) CH_3CHO and CH_3Br
    (b) $BrCH_2CHO$ and CH_3OH
    (c) $BrCH_2 - CH_2 - OCH_3$
    (d) $H_3C - CHBr - OCH_3$
15. The angle strain in cyclobutane is
    (a) 24°44
    (b) 29°16
    (c) 19°22
    (d) 9°44

Very Short:

1. Give different isomers of C_4H_{10} with their I.U.P.A.C. names.
2. Give the I.U.P.A.C. name of the lowest molecular weight alkane that contains a quaternary carbon.
3. Which of the following has the highest boiling point?
    (i) 2-methylpentane
    (ii) 2, 3 – dimethylbutane
    (iii) 2, 2-dimethylbutane.
4. Give the structure of the alkene (C_4H_8) which adds on HBr in the presence and in the absence of peroxide to give the same product C_4H_9Br.
5. How will you separate propene from propyne?
6. Name two reagents that can be used to distinguish \ between ethene and ethyne.
7. How will you detect the presence of unsaturation in an organic compound?
8. Arrange the following In order of increasing volatility: gasoline, kerosene, and diesel.
9. Arrange the following: HCl, HBr, HI, HF in order of decreasing reactivity towards alkenes.
10. Out of ethylene and acetylene which is more acidic and why?

Short Questions:

1. What are the various products expected when propane reacts with fuming nitric acid?
2. What is aromatization? How will you convert ^hexane into benzene?
3. Give the different conformations of ethane with their
    i. Sawhorse representation and
    ii. Newmann Projection formulae.
4. What are the relative stabilities of different conformations of ethane? Is it possible to isolate these at room temperature?
5. What is Saytzeff Rule? What are the expected products when 2-Bromobutane is dehydrohalogenation with ale. KOH?
6. Define Markownikov rule. Explain it with an example.

Long Questions:

1. Alkynes are less reactive than alkenes towards addition reaction even though they contain 2-7t bond. Give reason.
2. Why do addition reactions occur more readily with alkenes & alkynes than with aromatic hydrocarbons?
3. A Hydrocarbon As adds one mole of hydrogen in presence of platinum catalyst from n-Hexane. When A is oxidized vigorously with KMn04, a single carboxylic acid, containing three carbon atoms is isolated. Give the structure of A & explain.
4. How would you carry out the following conversion?
5. How would you convert the following compounds to benzene?
    (i) Acetylene
    (ii) Benzoic acid
    (iii) Hexane
    (iv) Benzene diazonium chloride

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

    Assertion (A): Toluene on Friedel Crafts methylation gives o– and p–xylene.

    Reason (R): CH_3-group bonded to benzene ring increases electron density at o– and p– position.

    (i) Both A and R are correct and R is the correct explanation of A.
    (ii) Both A and R are correct but R is not the correct explanation of A.
    (iii) Both A and R are not correct.
    (iv) A is not correct but R is correct.

2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

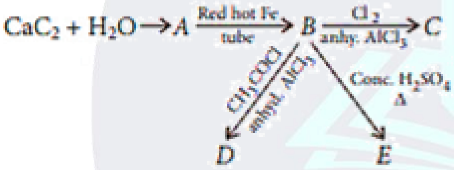
   Assertion (A): Nitration of benzene with nitric acid requires the use of concentrated sulphuric acid.

   Reason (R): The mixture of concentrated sulphuric acid and concentrated nitric acid produces the electrophile, NO_2

   (i) Both A and R are correct and R is the correct explanation of A.
   (ii) Both A and R are correct but R is not the correct explanation of A.
   (iii) Both A and R are not correct.
   (iv) A is not correct but R is correct.

Case Study Based Question:

1. Compound (A) is an important industrial feed stocks, but it's largest use as the fuel for the oxyacetylene torch. It is a colourless, foul smelling gas that burns in air with a yellow, sooty flame.



(1) Identify the product A.
   (a) Ethane
   (b) Ethyne
   (c) Ethene
   (d) Methane

(2) The compound (B) formed is:
   (a) Cyclohexane
   (b) Benzene
   (c) Hexane
   (d) Cyclopentane.

(3) The product E is:
   (a) Nitrobenzene
   (b) Benzene sulphonic acid
   (c) Both (a) and b
   (d) None of these.

(4) Identify the product 'D'.
   (a) Chlorobenzene
   (b) Bromobenzene
   (c) Toluene
   (d) Acetophenone

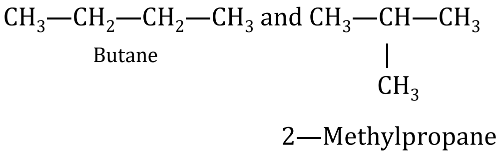
Answer Key

MCQ

1. (a) 1 – Phenyl – 2 – butene
2. (a) C = C
3. (a) Ethene
4. (a) 1, 4-dibromobutane
5. (c) n – Propyl bromide
6. (a) Neopentane
7. (c) They have a relatively high percentage of carbon
8. (c) But – 2 – ene
9. (b) There are three carbon-carbon single bonds and three carbon-carbon double bonds
10. (a) Wurtz Reaction
11. (a) Mesitylene
12. (a) Ethene
13. (a) Toluene
14. (d) $H_3C – CHBr – OCH_3$
15. (d) 9°44

Very Short Answer:

1.

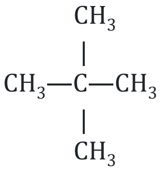


$CH_3—CH_2—CH_2—CH_3$ and $CH_3—\underset{\underset{CH_3}{|}}{CH}—CH_3$

Butane

2—Methylpropane

2.



$CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_3$

It is and its I.U.P.A.C. name is 2, 2-Dimethylpropane.

3. (i) 2—methyl pentane has the largest surface area and hence has the highest boiling point.

4. 2-Butene with structure $CH_3 - CH = CH — CH_3$ being symmetrical gives the same product, i.e., 2-bromobutane $CH_3 CH (Br) CH_2CH_3$.

5. Bypassing the mixture through ammoniacal $AgNO_3$ solution when propyne reacts while propene passes over.

6. Tollen's reagent | Ammoniacal $AgNO_3$ | and amm. CuCl solution.

7. Either by Baeyer's reagent

1%
|Alkaline $KMnO_4$|
Solution

or by Br, in CC14.

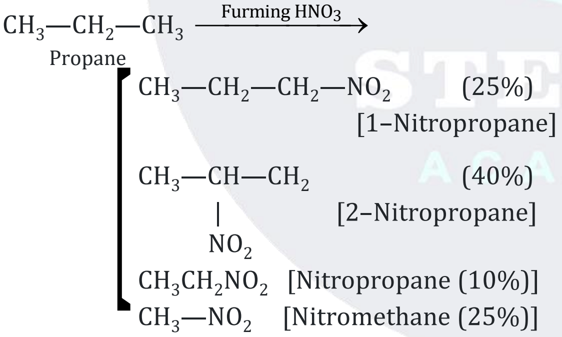
8. Diesel, kerosene, gasoline.

9. HF, HCl, HBr, HI..

10. Acetylene. Ethylene and acetylene have sp2, sp hybridized C atoms respectively. Due to the 50% S character of the C – H bond of acetylene rather than the 33% S-Character of the C – H bond in ethene, acetylene is more acidic.

Short Answer:

1. **Ans:**



$$\underset{\text{Propane}}{CH_3—CH_2—CH_3} \xrightarrow{\text{Furming } HNO_3}$$

$CH_3—CH_2—CH_2—NO_2$ (25%) [1–Nitropropane]

$CH_3—\underset{NO_2}{\underset{|}{CH}}—CH_2$ (40%) [2–Nitropropane]

$CH_3CH_2NO_2$ [Nitropropane (10%)]

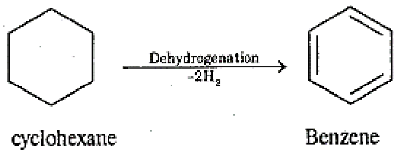
$CH_3—NO_2$ [Nitromethane (25%)]

2. **Ans:** Aromatization. It is the process that involves cyclization, isomerization, and dehydrogenation with the application of heat and catalyst to convert alkanes containing six or more carbon atoms into aromatic hydrocarbons.

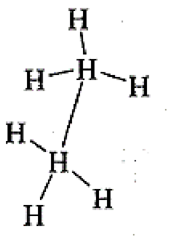
$CH_3—CH_2—CH_2—CH_2—CH_2—CH_3$

n-hexane

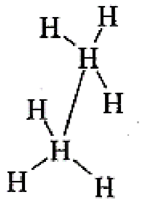
$$\xrightarrow[773 K, 10\text{-}20 \text{ atm. cyclisation-}H_2]{Cr_2O_3, V_2O_5 . MO_2O_3/Al_2O_3}$$



3. **Ans:** Sawhorse representation Newmann projection models



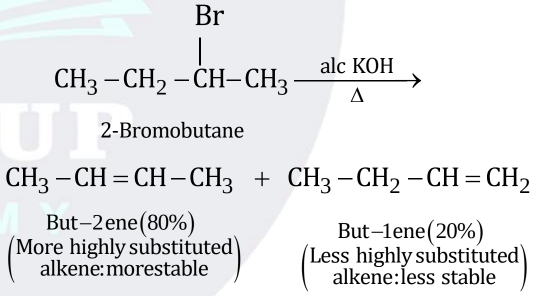
(Staggered form)



(Eclipsed from)

4. **Ans:** The staggering form of ethane is more stable than the eclipsed form because the force of repulsion between hydrogen atoms on adjacent C atoms is minimum. The energy difference between the staggered form and eclipsed form of ethane is just 12.55 kJ mol^{-1}. Therefore, it is not possible to separate these two forms of ethane at room temperature.

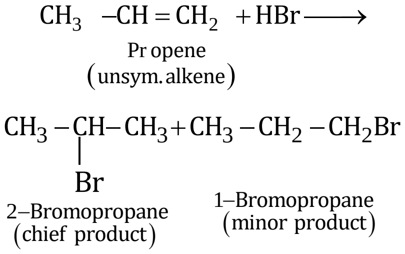
5. **Ans:** The staggering form of ethane is more stable than the eclipsed form because the force of repulsion between hydrogen atoms on adjacent C atoms is minimum. The energy difference between the staggered form and eclipsed form of ethane is just 12.55 kJ mol^{-1}. Therefore, it is not possible to separate these two forms of ethane at room temperature.



$$\underset{\text{2-Bromobutane}}{CH_3-CH_2-\overset{\overset{Br}{|}}{CH}-CH_3} \xrightarrow[\Delta]{\text{alc KOH}}$$

$$\underset{\substack{\text{But−2ene(80\%)}\\ \text{(More highly substituted}\\ \text{alkene:morestable)}}}{CH_3-CH=CH-CH_3} + \underset{\substack{\text{But−1ene(20\%)}\\ \text{(Less highly substituted}\\ \text{alkene:less stable)}}}{CH_3-CH_2-CH=CH_2}$$

6. **Ans:** Markownikov rule states. The negative part of the addendum adding to an unsymmetric alkene goes to that C atom of the double bond which is attached to a lesser number of C atoms.



$$\underset{\substack{\text{Pr opene}\\ \text{(unsym. alkene)}}}{CH_3 \ -CH=CH_2} + HBr \longrightarrow$$

$$\underset{\substack{\text{2–Bromopropane}\\ \text{(chief product)}}}{CH_3-\underset{\underset{Br}{|}}{CH}-CH_3} + \underset{\substack{\text{1–Bromopropane}\\ \text{(minor product)}}}{CH_3-CH_2-CH_2Br}$$

Long Answer:

1. **Ans:** This is due to
   1. greater electronegativity of sp-hybridized carbon of alkynes than sp^2 hybridized

carbon atoms of alkenes which holds the π-electrons of alkynes more tightly and

2. greater delocalization of π-electrons in alkynes (because of the cylindrical nature of their n electron cloud) than in alkenes. As a result, n electrons of alkynes are less easily available for addition reactions than those of alkenes.

Consequently, alkynes are less reactive than alkenes towards addition reactions.

2. Ans: The energy gained by forming two sigma bonds (of four sigma bonds) more than compensates for the loss of one or two n bonds when addition occurs to an alkene or alkyne. However, in aromatic hydrocarbons, the aromatic ring is specially stabilized by the delocalization of n electrons about the ring.

It, therefore, requires substantial activation energy to cause the loss of its aromatic character. The most usual reaction in arenes is thus substitution rather than addition, since substitution does not result in loss of aromatic character.

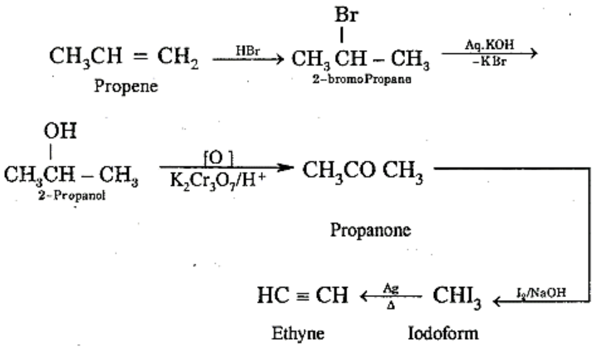
3. Ans:

1. Since hydrocarbon A adds one molecule of H_2 in presence of platinum to form n-hexane. A must be a hexene.
2. Since A on vigorous oxidation with $KMnO_4$ gives a single carboxylic acid containing three carbon atoms, therefore, A must be asymmetrical hexene i.e., hex-3-ene.

$$\underset{(A)}{CH_3CH_2CH=CHCH_2CH_3} \xrightarrow[KMnO_4]{O} \underset{\text{propanoic acid}}{2CH_3CH_2COOH}$$

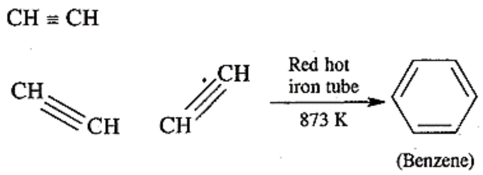
Thus, the given hydrocarbon A is hex-3-ene.

4. Ans: Propene to Ethyne

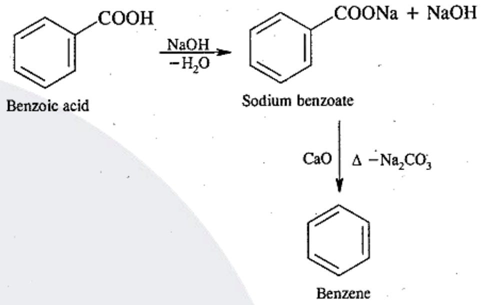


5. Ans:

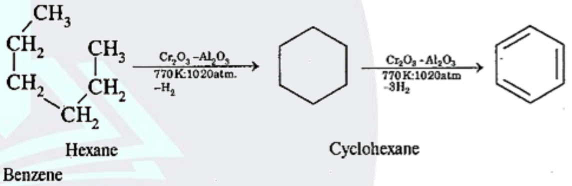
(i) Acetylene into benzene. Ethyne (Acetylene) in passing through a red-hot iron tube at 873 K undergoes cyclic polymerization as shown below.



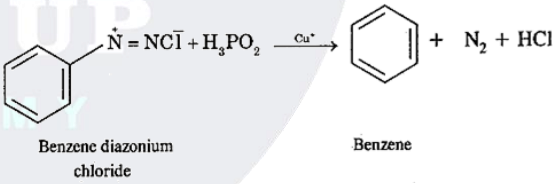
(ii) Benzoic acid into benzene



(iii) Hexane into benzene



(iv) Benzene diazonium chloride into benzene



Assertion Reason Answer:

1. (i) Both A and R are correct and R is the correct explanation of A.
2. (i) Both A and R are correct and R is the correct explanation of A.

Case Study Answer:

1. **Answer:**

(1) (b) Ethyne

(2) (c) Hexane

(3) (b) Benzene sulphonic acid

(4) (d) Acetophenone

Environmental Chemistry

14

Introduction

Interrelation of biological, social, economical, physical and chemical studies with our surrounding is called environmental studies. Environmental pollution is the greatest health hazard all over the world. Environmental chemistry deals with the study of the origin, transport, reactions, effects and fates of chemical species in the environment.

An undesirable change in physical, chemical or biological characteristics of air, water and land that is harmful to human life and other living organisms, living conditions, cultural assets, industrial progress and harms our resources is called pollution.

Environmental Pollution

Undesirable changes that have harmful effects on plants, animals and human beings in our surrounding is called environmental pollution.

Pollutant

The substance which causes pollution and is harmful for environment is called pollutant. Pollutants are of two types:

1. **Biodegradable**

   Those substances which are degraded rapidly by natural process or artificial methods are called biodegradable pollutants. Ex- discarded vegetables.

2. **Non-biodegradable**

   Those substances which degrade at very slow rate or does not degrade by natural biological process, for example, DDT, arsenic salts of heavy metals, radioactive materials and plastics are non-biodegradable pollutants.

Atmospheric Pollution

Lowest layer of atmosphere is troposphere which have dust, water vapour and clouds, it contains dust, water vapour and clouds while stratosphere contains ozone. Atmospheric pollution includes both troposphere and stratosphere pollution.

Tropospheric Pollution

Tropospheric pollution occurs due to the presence of undesirable solid or gaseous particles in the air.

1. **Gaseous air pollutants:**
   i. **Oxides of Sulphur:** Oxides of sulphur are produced when sulphur containing fossil fuel is burnt. The most common species, sulphur dioxide, is a gas that is poisonous to both animals and plants. It has been reported that even a low concentration of sulphur dioxide causes respiratory diseases e.g., asthma, bronchitis, emphysema in human beings. Sulphur dioxide causes irritation to the eyes, resulting in tears and redness.

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

   ii. **Oxides of Nitrogen:** Mainly produced by combustion of fossil fuels at high temperature in automobile engines mainly NO and NO_2.

iii. These produce reddish brown haze or brown air NO_2 is more dangerous than NO. These oxides can cause pulmonary oedema, dilation of arteries, eye irritation, heart problems, injury to liver and kidneys and also causes acid rains.

$$N_2 + O_2 \longrightarrow 2NO$$

$$2NO + O_2 \longrightarrow 2NO_2$$

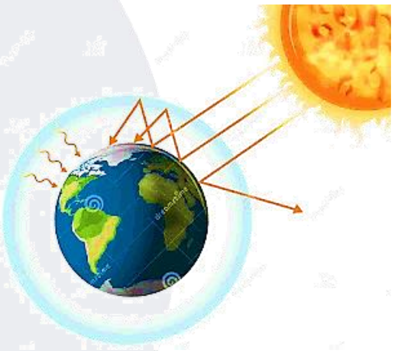
iv. **Hydrocarbons**: Produced naturally (e.g., marsh gas) as well as due to incomplete combustion. These are carcinogenic and causes irritation of mucous membrane, eyes. They causes ageing, breakdown of tissues, shedding of flower, leaves and twigs in plants.

v. **Carbon monoxide:** It is colourless, odourless gas. It is produced by incomplete combustion of fuels, naturally it is produced by oceans or by decaying of organic matter by bacteria. It is poisonous because it combines with hemoglobin to form 300 more times stable carboxyhemoglobin which reduces oxygen-carrying capacity of blood and results into giddiness, headache, decreased vision, cardiovascular malfunction and asphyxia. Cigarette smoke also contains a lot of CO which induces premature birth deformed babies and spontaneous abortions in pregnant women.

vi. **Carbon dioxide:** It is produced naturally by volcanic eruptions, respiration. It is also produced by burning of fossil fuels. Increased level of CO_2 is controlled by green plants during photosynthesis. It is a greenhouse gas and responsible for global warming. It causes headache nausea and asphyxiation.

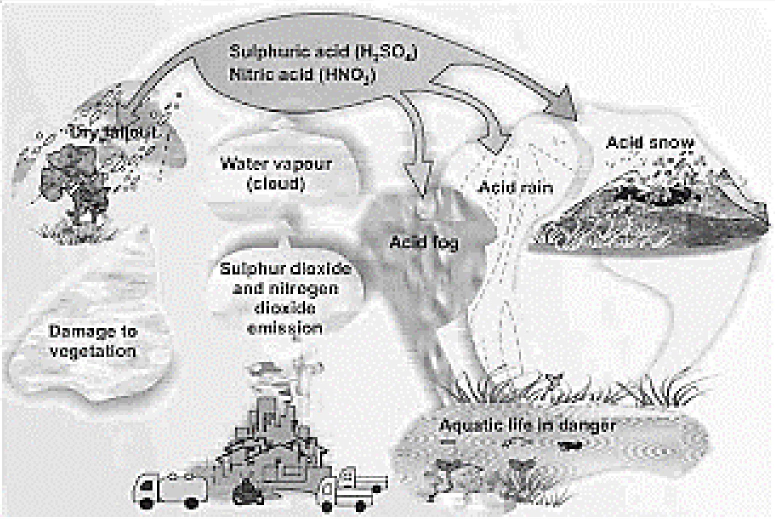
2. Greenhouse Effect

This effect was discovered by Fourier and the term was coined by Arrhenius. 75% of solar radiation is absorbed by earth surface and remaining is reflected back. Some of which is absorbed by greenhouse gases such as carbon dioxide, methane, ozone, chlorofluorocarbon compounds (CFCs) and water vapour in the atmosphere which increases temperature of atmosphere is called greenhouse effect.



3. Acid Rain

When the pH value of the rain water drops below 5.6, it is known as acid rain. Acid rain is a byproduct of a variety of human activities that emit the oxides of sulphur and nitrogen in the atmosphere.



$$2SO_2(g) + O_2(g) + 2H_2O(l) \longrightarrow 2H_2SO_4(aq)$$

Stratospheric Pollution

1. Ozone Hole

Depletion in the concentration of ozone over a restricted area as over Antarctica is called ozone hole. Stratospheric clouds are formed over Antarctica.

Molecular oxygen splits into free oxygen atoms by UV radiations which combine with molecular oxygen to form ozone.

$$O_2(g) \longrightarrow [O](g) + [O](g)$$

$$[O](g) + O_2(g) \longrightarrow O_3(g)$$

As ozone is thermodynamically unstable hence, there exists dynamic equilibrium between its decomposition and formation. Ultraviolet radiations dissociate chlorofluorocarbon to give chlorine-free radical, which combines with ozone to form chlorine monoxide radical which combines with free oxygen to form more chlorine-free radicals.

$$CF_2Cl_2 \longrightarrow [C]F_2Cl + [Cl]$$

$$[Cl] + O_3 \longrightarrow Cl[O] + O_2$$

$$2Cl[O] + O_3 \longrightarrow 2[Cl] + 2O_2$$

Effects of Depletion of The Ozone Layer:

Bad ozone is formed in troposphere that harms plants and animals while good ozone is formed in stratosphere which acts as shield. UV rays can enter in earth's atmosphere.

- It is harmful as can cause skin cancer.
- It increases transpiration hence decreases soil moisture.
- It damages paints and fibres, causing them to fade faster.

Water Pollution

Any unwanted change which detiorate quality of water and make it unfit for drinking is called water pollution. Pollution of water originates from human activities.

Causes of Water Pollution

1. Organic matter such as leaves, grass, trash etc. as well as excessive phytoplankton growth in water causes water pollution as this matter is decomposed through microbial activity is known as putrescibility which requires oxygen. Degree of impurity of water due to organic matter is measured in terms of Biochemical Oxygen Demand (BOD).
2. **Pathogens:** Disease-causing agents are called pathogens e.g., viruses, bacteria, protozoa, helminths, algae etc. Human excreta contains *E.coli* and Streptococcus faecalis bacteria which cause gastrointestinal diseases.
3. **Chemical pollutants:** These are of two types, inorganic and organic.
4. Inorganic pollutants constitute acids, salts, heavy metals such as Cd, Hg, Ni etc. Heavy metals can damage central nervous system, liver and kidneys.
5. Organic pollutants constitute, pesticides, petroleum pollutants, PCBs, detergents, fertilizers etc. PCBs (Polychlorinated Biphenyls) are carcinogenic and phosphatic fertilizers increase algae growth. Acidic water is harmful for aquatic life as well as for drinking.

Soil Pollution

It is unfavourable alteration of soil by addition or removal of substances and factors which decrease soil productivity, quality of plants and ground water is called soil pollution. Mainly caused by chemicals added into soil as pesticides, herbicides and fertilizers for better productivity.

Causes of Soil Pollution

1. **Pesticides:** These are actually synthetic toxic chemicals with ecological repercussions. These are used in killing pathogens, pests and in inhibiting unwanted growth in agriculture, horticulture, forestry and water.
2. **Fertilizers:** Excessive use of fertilizers decreases natural microflora hence detiorate soil. Therefore, now a days organic farming is encouraged which involves organic pesticides, biofertilizers and disease resistant varieties.

3. **Industrial wastes:** These are both solid and liquid and are dumped over the soil. These contain toxic chemicals like mercury, copper, zinc, lead, cadmium, cyanides, acid, alkalies etc.

Strategies to Control Environmental Pollution

Two sources of environment pollutant are household waste and industrial waste. Following method can be used to control them.

1. **Recycling:** Waste are recycled into manufacturing of new material. For example, scrap iron, broken glass, clothes can be made from recycled plastic waste and soon becomes available in market. We can also recover energy from burning combustible waste.
2. **Digestion:** Waste material can be degraded by anaerobic micro-organisms in absence of air. It can be used to produce electricity. First biodegradable and non-biodegradable waste are separated then biodegradable wastes are mixed with water and cultured by bacterial species which produce methane.
3. **Dumping:** Sewage sludge acts as fertilizer because it contains nitrogen and phosphorus hence, it is dumped in land areas which increases soil fertility.

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. Utilization of existing knowledge base for reducing the chemical hazards along with the development activities are the foundation of green chemistry.

Summary

1. Environmental pollution causes undesirable changes in our surrounding that have harmful effect on plants, animals and human beings.
2. Atmospheric pollution is studied as tropospheric pollution and stratospheric pollution.
3. Smog and global warming take place due to tropospheric pollution.
4. Stratospheric pollution causes depletion of ozone layer.
5. Water pollution is caused by pathogens, organic wastes and chemical pollutants.
6. Soil pollution is caused by insecticides, pesticides and herbicides.
7. Industrial waste is of two type, biodegradable and non-biodegradable.
8. Green chemistry is a way of thinking and is about to utilize the existing knowledge and principles of chemistry and other sciences to reduce the adverse impact on environment.

Class : 11th Chemistry
Chapter- 14: Environmental Chemistry

Causes of water pollution:
(i). Pathogens which cause diseases. (Escherichia coli, Streptococcus faecalis)
(ii). Organic Wastes: (Leaves, grass, trash)
(iii). Chemical Pollutants: Heavy metals, acids from mine drainage, salts from different sources, petroleum products, fertilizers and industrial chemicals.
Eutrophication: Process in which nutrient enriched water bodies support a dense plant population which kills animals life and loss of biodiversity. International standards for Drinking water (i). Fluoride: Excess fluoride (over 10 ppm) causes harmful effects to bones and teeths.
(ii). Lead: Prescribed upper limit in drinking Water is about 50ppm.
(iii). Sulphate: >500ppm causes laxative effect.
(iv). Nitrate: Maximum limit in water is 50ppm.
(v). Other metals: Fe, Mn, Al, Cu, Zn, Cd.

Pesticides (DDT)
Herbicidies
Industrial Waste:
(i). Biodegradable wastes are generated by cotton mills, food processing units, paper mills and textile factories.
(ii). Non-biodegradable wastes are generated by thermal power plants, integrated iron and steel plants, fertilizer industries, etc.
(iii). Control:
(i). Use of manures
(ii). Use of bio-fertilizers
(iii). Proper sewage system
(iv) Salvage and recycling

It is a naturally occurring phenomenon responsible for heating of earth's surface and atmosphere due to presence of certain gases in the atmosphere.
Global warming is the gradual and continuos increase in average temperature of surface of the earth due to increase in concentrations of greenhouse gases $(CO_2, CFCs, CH_4)$

Troposphere
~10 Km from sea level

Greenhouse Effect

Stratosphere
Between 10 and 50 km above sea level

Soil Pollution

Water Pollution

Environmental Chemistry

Deals with the study of origin, transport, reactions, effects and fates of chemical species in the environment

Stratospheric Pollution:
Ozone present in upper stratosphere protects us from cancer causing harmful uv radiations.
Depletion of Ozone layer:

$$Cl\dot{O}_{(g)} + NO_{2(g)} \longrightarrow ClONO_{2(g)}$$

$$\dot{C}l_{(g)} + CH_{4(g)} \longrightarrow \dot{C}H_{3(g)} + HCl_{(g)}$$

$$ClONO_{2(g)} + H_2O_{(g)} \longrightarrow HOCl_{(g)} + HNO_{3(g)}$$

$$ClONO_{2(g)} + HCl_{(g)} \longrightarrow Cl_{2(g)} + HNO_{3(g)}$$

$$HOCl_{(g)} \xrightarrow{h\nu} \dot{O}H_{(g)} + \dot{C}l_{(g)}$$

$$Cl_{2(g)} \xrightarrow{h\nu} 2\dot{C}l_{(g)}$$

Atmospheric Pollution

Strategies to Control
(i) Waste Management
(ii) Collection and Disposal

Environmental Pollution
Effect of undesirable changes in our surroundings that have harmful effects on plants, animals and human beings)
Acid Rain (when pH of the rain after drops below 5.6.)

Tropospheric Pollution:
Occurs due to the presence of undesirable solid or gaseous particles in the air.
Pollutants presents in Troposphere:
1. Gaseous air pollutants:
(a). Oxides of sulphur produced when sulphur containing fossil fuel is burnt. It causes respiratory diseases.
(b). Oxides of Nitrogen: At high altitudes when lightning strikes, dinitrogen and dioxygen combine to form oxides of hydrogen. In an automobile engine, when fossil fuel is burnt, dinitrogen and dioxygen combine to form NO and NO_2
(c). Hydrocarbons: Formed by incomplete combustion of fuel used in automobiles.
They are carcinogenic and harm plants also.
(d). Oxides of Carbon: CO, CO_2
2. Particulate pollutants: (Minute solid particles or liquid droplets in air present in vehicle emissions, smoke particles from fires, dust particles and ash from industries).
(a). Smog: Smoke + Fog
Types of smog:
(i). Classical smog occurs in cool humid climate. It is a mixture of smoke, fog and sulphur dioxide.
(ii). Photochemical smog occurs in warm, dry and sunny climate. It has high concentration of oxidising agents. It contains ozone, nitric oxide, acrolain, formaldehyde and PAN.
It causes serious health problems.

Biochemical Oxygen Demand (BOD)
Amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water.

Green Chemistry
It is a way of thinking and utilizing the existing knowledge and principles of chemistry and other sciences to reduces the adverse impact in environment.
In Daily life:
(i)Dry cleaning of clothes.
(ii)Bleaching of paper
(iii) Synthesis of chemicals

Important Questions

Multiple Choice Questions

1. Photochemical smog normally does not contain
   (a) Chlorofluorocarbons
   (b) Peroxyacetyl nitrate
   (c) Ozone
   (d) Acrolein
2. Depletion of the ozone layer is caused due to
   (a) Ferrocene
   (b) Fullerenes
   (c) Freons
   (d) Polyhalogens
3. Find the incorrect statement
   (a) BOD value of clean water is less than 5 ppm
   (b) Drinking water pH should be between 5.5-9.5
   (c) carbon, sulphur and nitrogen oxides are the most widespread air pollutants
   (d) dissolved oxygen concentration below 5 ppm is ideal for the growth of fish
4. Find the secondary pollutant among these
   (a) PAN
   (b) N_2O
   (c) SO_2
   (d) CO_2
5. The reaction responsible for the radiant energy of the Sun is
   (a) nuclear fission
   (b) nuclear fusion
   (c) chemical reaction
   (d) combustion
6. Alum's capacity to purify water is due to
   (a) softens hard water
   (b) pathogenic bacteria get destroyed
   (c) impurities' coagulation
   (d) it improves taste
7. The coldest region of the atmosphere
   (a) Troposphere
   (b) Thermosphere
   (c) Stratosphere
   (d) Mesosphere
8. Which of the oxide of nitrogen is not a common pollutant?
   (a) N_2O_5
   (b) N_2O
   (c) NO
   (d) NO_2
9. The compound essential for the process of photosynthesis has this element
   (a) Ca
   (b) Ba
   (c) Fe
   (d) Mg
10. In the air, N_2 and O_2 occur naturally but they do not react to form oxides of nitrogen because
    (a) oxides of nitrogen are unstable
    (b) catalyst is required for the reaction
    (c) the reaction is endothermic
    (d) N_2 and O_2 do not react with each other
11. This about carbon monoxide is incorrect.
    (a) It is produced due to incomplete combustion
    (b) The carboxyhaemoglobin (haemoglobin found to CO) is less stable than oxyhaemoglobin
    (c) It reduces the oxygen-carrying ability of blood
    (d) It forms carboxyhaemoglobin
12. This is a sink for CO
    (a) Haemoglobin
    (b) Oceans
    (c) Micro-organisms present in the soil
    (d) Plants
13. DDT is
    (a) Nitrogen containing insecticide
    (b) Biodegradable pollutant
    (c) Non-Biodegradable pollutant
    (d) An antibiotic

14. Which of the following techniques is/are used in controlling water pollution?
    (a) Reverse osmosis
    (b) Ion exchange process
    (c) Adsorption process
    (d) All of these
15. Which of the following pollutants cannot be degraded by natural process?
    (a) Heavy metals
    (b) DDT
    (c) Nuclear waste
    (d) All of these

Very Short:

1. What is the troposphere?
2. Name some gaseous air pollutants.
3. What are the diseases caused by sulphur dioxide?
4. List gases that are responsible for the greenhouse effect?
5. What is the effect of CFC's on the ozone layer?
6. What is the greenhouse effect?
7. Which disease is caused due to ozone layer depletion?
8. What is smog?
9. The London smog is caused in which season and time of the day?
10. Name two gases that form acid rain.

Short Questions:

1. What is the role of the ozone layer in the stratosphere?
2. What includes stratospheric pollutants? Give examples.
3. Why is carbon monoxide considered to be poisonous?
4. What are the ill effects of hydrocarbons?
5. Give one main reason for ozone depletion?
6. Which zone is called the ozonosphere?
7. What is the 'greenhouse effect'? How does it affect the global climate?

Long Questions:

1. What is the difference between London (classical) smog and photochemical (Los Angeles) smog?
2. Explain how does greenhouse effect cause global warming.
3. Green plants use carbon dioxide for photosynthesis and return oxygen to the atmosphere, even then carbon dioxide is considered to be responsible for greenhouse effect. Explain why?

Assertion Reason Questions:

1. In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): Greenhouse effect was observed in houses used to grow plants and these are made of green glass.

   Reason (R): Greenhouse name has been given because glass houses are made of green glass.

   (i) Both A and R are correct and R is the correct explanation of A.
   (ii) Both A and R are correct but R is not the correct explanation of A.
   (iii) Both A and R are not correct.
   (iv) A is not correct but R is correct.

2. In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): The pH of acid rain is less than 5.6

   Reason (R): Carbon dioxide present in the atmosphere dissolves in rain water and forms carbonic acid.

   (i) Both A and R are correct and R is the correct explanation of A.
   (ii) Both A and R are correct but R is not the correct explanation of A.
   (iii) Both A and R are not correct.
   (iv) A is not correct but R is correct.

Answer Key

MCQ

1. (a) Chlorofluorocarbons
2. (c) Freons
3. (d) dissolved oxygen concentration below 5 ppm is ideal for the growth of fish
4. (a) PAN
5. (b) nuclear fusion
6. (c) impurities' coagulation
7. (d) Mesosphere
8. (a) N_2O_5
9. (d) Mg
10. (c) the reaction is endothermic
11. (b) The carboxyhaemoglobin (haemoglobin found to CO) is less stable than oxyhaemoglobin
12. (c) Microorganisms present in the soil
13. (c) non-Biodegradable pollutant
14. (d) All of these
15. (d) All of these

Very Short Answer:

1. **Ans:** The troposphere is the lowest layer of the atmosphere, where humans and other creatures live. It reaches a height of approximately 10 kilometres above sea level.
2. **Ans:** Sulfur, nitrogen, and carbon oxides, hydrogen sulphide, hydrocarbons, ozone, and other oxidants are examples of gaseous air pollution.
3. **Ans:** In humans, sulphur dioxide causes respiratory disorders such as asthma, bronchitis, and emphysema. In addition, sulphur dioxide causes eye irritation, resulting in tears and redness.
4. **Ans:** The gases responsible for the greenhouse effect are: carbon dioxide, methane, water vapours, nitrous oxide, CFC's.
5. **Ans:** CFC's also known as chlorofluorocarbons tend to damage the ozone layer and creates holes in the ozone layer.
6. **Ans:** The greenhouse effect is the process through which solar energy is absorbed by greenhouse gases instead of being reflected back into space. This keeps the earth's surface warm and prevents it from freezing.
7. **Ans:** Skin cancer is caused when the ozone layer is depleted from the atmosphere. The ultraviolet rays from the sun reach the earth through the holes present in the ozone layer and cause skin related diseases.
8. **Ans:** Smog is a type of air pollution that was named from the combination of smoke and fog in the atmosphere. Smog is created by a mixture of smoke and sulphur dioxide and occurs when significant amounts of coal are burned in a certain area.
9. **Ans:** The London smog is caused by the hot weather in the summer, especially in the afternoon.
10. **Ans:** Acid rain is caused by the oxides of sulphur and nitrogen and the gases involved in it are sulphur dioxide (SO_2) and nitrogen dioxide (NO_2).

Short Answer:

1. **Ans:** The existence of ozone in the stratosphere blocks 99.5 per cent of the sun's damaging ultraviolet (UV) light from reaching the earth's surface, shielding people and other animals from its destructive effects.
2. **Ans:** The outcome of stratospheric pollution is the depletion of the ozone layer in the stratosphere, which allows dangerous ultraviolet light to reach the earth. This depletion is caused by the existence of chlorofluorocarbons in the environment.
3. **Ans:** When carbon monoxide is released into the atmosphere, it is inhaled by animals and humans. Inside the body, carbon monoxide links to haemoglobin to create carboxyl–haemoglobin, which is 300 times more stable than oxygen – haemoglobin. This oxygen deprivation causes headaches, blurred vision, anxiety, and cardiovascular problems.
4. **Ans:** Hydrocarbons are carcinogenic i.e; they cause cancer. Plants are harmed by them because they cause ageing, tissue degradation, and the dropping of leaves, flowers, and trigs.
5. **Ans:** The major cause of ozone layer depletion is chlorofluorocarbons (CFCs). Solvents, spray aerosols, freezers, and air conditioners, among other things, emit ultraviolet radiation. Ultraviolet radiations break down chlorofluorocarbon molecules in the stratosphere, releasing chlorine atoms.

6. **Ans:** The ozonosphere is an area or zone in the stratospheric layer of the atmosphere with a high concentration of ozone gas molecules.

7. **Ans:** The greenhouse effect is the warming of the planet or global warming caused by the re-emission of sun's energy collected by the earth, absorption by CO_2 molecules and H_2O vapours existing in the atmosphere near the earth's surface, and then radiation back to the ground. Greenhouse affects the climate. If the pace at which solar radiation reaches the earth continues, the entire global climate will alter dramatically.

Long Answer:

1. **Ans:**

Classical (London) smog	Photochemical (Los Angeles) Smog
1. This type of smog was first observed in London in 1952.	1. This type of smog was first observed in Los Angeles in 1950.
2. It is formed due to the presence of SO_2 and humidity in the air which combines to form H_2SO_4 fog which gets deposited on the particulates.	2. It is formed due to a photochemical reaction taking place when the air contains NO_2 and hydrocarbons.
3. It involves smoke and fog.	3. It does not involve any smoke or fog. The word smog is a misnomer here.
4. It is formed in the months of winter particularly in the morning hours when the temperature is low.	4. It is formed during the months of summer during the afternoon when there is bright sunlight so that photochemical reaction can take place.
5. It causes a problem in the lungs.	5. It causes irritation in the eyes.
6. It is reducing in character.	6. It is oxidising in character.

2. **Ans:** The greenhouse effect is defined as the trapping of the sun's heat in the lower atmosphere as a result of increased pollution-causing chemicals such as carbon dioxide. Water vapour, carbon dioxide (CO_2), methane, nitrous oxides, and chlorofluorocarbons are some of the gases that contribute to the greenhouse effect (CFCs).

   The sun's radiation is partially absorbed by the earth, with the remainder being reflected back into the atmosphere and escaping. However, greenhouse gases form a blanket in the atmosphere, trapping radiation and preventing it from leaving. As a result, the earth's temperature rises, resulting in global warming.

3. **Ans:** Carbon dioxide is a naturally occurring component of the atmosphere that is essential for all plant life. It makes up around 0.033 per cent of the atmosphere's volume. It aids in maintaining the earth's temperature, which is necessary for living beings. CO_2 balance is maintained in the atmosphere because CO_2 is created by respiration, fossil fuel combustion, and limestone disintegration, but it is also consumed by plants during photosynthesis.

   However, human activities have disrupted this equilibrium, and CO_2 levels in the atmosphere are rising. This is because deforestation has increased by around 25% in the last century. The average temperature of the earth has risen by 0.4°C to 0.8°C over the last approximately 120 years. According to current estimates, a doubling CO_2 concentration will result in a temperature increase of between 1.0°C and 3.5°C. The contribution of CO_2 to the greenhouse effect is 50%, and the contribution of other trace gases is similarly about 50%.

Assertion Reason Answer:

1. **Ans:**

   (iii) Both A and R are not correct.

   (ii) Both A and R are correct but R is not the correct explanation of A.

❖❖