पु॑ना International School
Shree Swaminarayan Gurukul, Zundal

Class -XI

Chemistry

Specimen Copy

Year- 2021-22

INDEX

SOME BASIC CONCEPTS OF CHEMISTRY

1. CHEMISTRY

Chemistry is defined as the study of the composition, properties and interaction of matter. Chemistry is often called the central science because of its role in connecting the physical sciences, which include chemistry, with the life sciences and applied sciences such as medicine and engineering.

Various branches of chemistry are

1.1 Physical chemistry

The branch of chemistry concerned with the way in which the physical properties of substances depend on and influence their chemical structure, properties, and reactions.

1.2 Inorganic chemistry

The branch of chemistry which deals with the structure, composition and behavior of inorganic compounds. All the substances other than the carbon-hydrogen compounds are classified under the group of inorganic substances.

1.3 Organic chemistry

The discipline which deals with the study of the structure, composition and the chemical properties of organic compounds is known as organic chemistry.

1.4 Biochemistry

The discipline which deals with the structure and behavior of the components of cells and the chemical processes in living beings is known as biochemistry.

1.5 Analytical chemistry

The branch of chemistry dealing with separation, identification and quantitative determination of the compositions of different substances.

2. MATTER

Matter is defined as any thing that occupies space possesses mass and the presence of which can be felt by any one or more of our five senses.

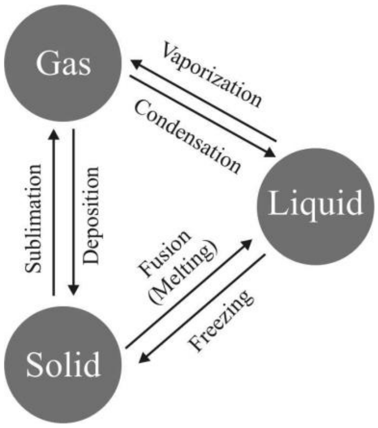
Matter can exist in 3 physical states viz. solid, liquid, gas.

Solid - a substance is said to be solid if it possesses a definite volume and a definite shape, e.g., sugar, iron, gold, wood etc.

Liquid- A substance is said to be liquid, if it possesses a definite volume but no definite shape. They take up the shape of the vessel in which they are put, e.g., water, milk, oil, mercury, alcohol etc.

Gas- a substance is said to be gaseous if it neither possesses definite volume nor a definite shape. This is because they fill up the whole vessel in which they are put, e.g., hydrogen, oxygen etc.

The three states are interconvertible by changing the conditions of temperature and pressure as follows

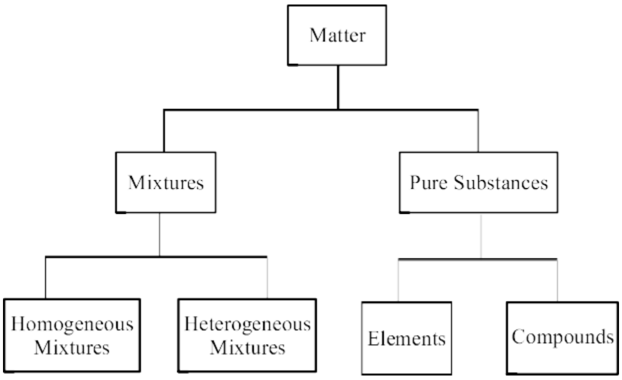


3. CLASSIFICATION OF MATTER AT MACROSCOPIC LEVELL

At the macroscopic or bulk level, matter can be classified as

(a) mixtures (b) pure substances.

These can be further sub-divided as shown below



Classification of matter

(a) Mixtures : Amixture contains two or more substances present in it (in any ratio) which are called its components. A mixture may be homogeneous or heterogeneous.

Homogeneous mixture- in homogeneous mixture the components completely mix with each other and its composition is uniform throughout i.e it consist of only one phase. Sugar solution and air are thus, the examples of homogeneous mixtures.

Heterogeneous mixtures- In heterogeneous mixture the composition is not uniform throughout and sometimes the different phases can be observed. For example, grains and pulses along with some dirt (often stone) pieces, are heterogeneous mixtures.

Note...

Any distinct portion of matter that is uniform throughout in composition and properties is called a Phase.

(b) Pure substances :- A material containing only one substance is called a pure substance.

Note...

In chemistry, a substance is a form of matter that has constant chemical composition and characteristic properties. It cannot be separated into components by physical separation methods, i.e. without breaking chemical bonds. They can be solids, liquids or gases.

Pure substances can be further classified into elements and compounds.

Element- An element is defined as a pure substance that contains only one kind of particles. Depending upon the physical and chemical properties, the elements are further subdivided into three classes, namely (1) Metals (2) Non-metals and (3) Metalloids.

Compound- A compound is a pure substance containing two or more than two elements combined together in a fixed proportion by mass. Further, the properties of a compound are completely different from those of its constituent elements. Moreover, the constituents of a compound cannot be separated into simpler substances by physical methods. They can be separated by chemical methods.

4. PROPERTIES OF MATTER

Every substance has unique or characteristic properties. These properties can be classified into two categories – physical properties and chemical properties.

4.1 Physical Properties

Physical properties are those properties which can be measured or observed without changing the identity or the composition of the substance. Some examples of physical properties are color, odor, melting point, boiling point, density etc.

4.2 Chemical properties

Chemical properties are those in which a chemical change in the substance occurs. The examples of chemical properties are characteristic reactions of different substances; these include acidity or basicity, combustibility etc.

5. MEASUREMENT

5.1 Physical quantities

All such quantities which we come across during our scientific studies are called Physical quantities. Evidently, the measurement of any physical quantity consists of two parts

(1) The number, and (2) The unit

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

5.2 S.I. UNITS

The International System of Units (in French Le Systeme International d'Unités – abbreviated as SI) was established by the 11th General Conference on Weights and Measures (CGPM from Conference Generale des Poids at Measures). The CGPM is an inter governmental treaty organization created by a diplomatic treaty known as Meter Convention which was signed in Paris in 1875.

The SI system has seven base units and they are listed in table given below.

These units pertain to the seven fundamental scientific quantities. The other physical quantities such as speed, volume, density etc. can be derived from these quantities. The definitions of the SI base units are given below :

Definitions of SI Base Units

Unit of length	metre	The metre is the length of the path travelled by light in vacuum during a time interval of 1/299 792 458 of a second.
Unit of mass	Kilogram	The kilogram is the unit of mass; it is equal to the mass of the internationl prototype of the kilogram.
Unit of time	second	The second is the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium-133 atom.
Unit of electric current	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.
Unit of thermodynamic temperature	kelvin	The kelvin, unit of thermodynamic temperature, is the fraction 1/273. 16 of the thermodynamic temperature of the triple point of water.
Unit of amount of substance	mole	1. 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.". 2. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.
Unit of luminous intensity	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.

Note...

The mass standard is the kilogram since 1889. It has been defined as the mass of platinum-iridium (Pt-Ir) cylinder that is stored in an airtight jar at International Bureau of Weights and Measures in Sevres, France. Pt-Ir was chosen for this standard because it is highly resistant to chemical attack and its mass will not change for an extremely long time.

6. SOME IMPORTANT DEFINITION

6.1 Mass and Weight

Mass of a substance is the amount of matter present in it while weight is the force exerted by gravity on an object. The mass of a substance is constant whereas its weight may vary from one place to another due to change in gravity. The SI unit of mass is the kilogram (kg). The SI derived unit (unit derived from SI base units) of weight is newton.

6.2 Volume

Volume is the quantity of three-dimensional space enclosed by some closed boundary, for example, the space that a substance (solid, liquid, gas, or plasma) or shape occupies or contains. Volume is often quantified numerically using the SI derived unit, the cubic meter.

6.3 Density

The mass density or density of a material is defined as its mass per unit volume. The symbol most often used for density is p (the lower case Greek letter rho). SI unit of density is $kg\ m^{-3}$.

6.4 Temperature

Temperature is a physical property of matter that quantitatively expresses the common notions of hot and cold. There are three common scales to measure temperature — °C (degree celsius), °F (degree fahrenheit) and K (kelvin). The temperature on two scales is related to each other by the following relationship:

$$°F = 9/5\ (°C) + 32$$

$$K = °C + 273.15$$

7. LAW OF CHEMICAL COMBINATION

7.1 Law of conservation of mass

"In a chemical reaction the mass of reactants consumed and mass of the products formed is same, that is mass is conserved." This is a direct consequence of law of conservation of atoms. This law was put forth by Antoine Lavoisier in 1789.

7.2 Law of Constant / Definite Proportions

The ratio in which two or more elements combine to form a compound remains fixed and is independent of the source of the compound. This law was given by, a French chemist, Joseph Proust.

7.3 Law of Multiple Proportions

When two elements combine to form two or more compounds then the ratio of masses of one element that combines with a fixed mass of the other element in the two compounds is a simple whole number ratio. This law was proposed by Dalton in 1803.

7.4 Law of Reciprocal Proportions

When three elements combine with each other in combination of two and form three compounds then the ratio of masses of two elements combining with fixed mass of the third and the ratio in which they combine with each other bear a simple whole number ratio to each other. This Law was given by Richter in 1792.

7.5 Gay Lussac's Law of Gaseous Volumes

This law was given by Gay Lussac in 1808. He observed that when gases combine or are produced in a chemical reaction they do so in a simple ratio by volume provided all gases are at same temperature and pressure.

7.6 Avogadro Law

In 1811, Avogadro proposed that equal volumes of gases at the same temperature and pressure should contain equal number of molecules.

8. DALTON'S ATOMIC THEORY

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

1. Matter consists of indivisible atoms.
2. All the 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 reorganization of atoms. These are neither created nor destroyed in a chemical reaction.

9. ATOM

Atom is the smallest part of an element that can participate in a chemical reaction. {Note : This definition holds true only for non-radioactive reactions}

9.1 Mass of an Atom

There are two ways to denote the mass of atoms.

9.2 Method 1

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. = 1/12th of the mass of one C^{12} atom

9.3 Method 2

Mass of 6.022×10^{23} atoms of that element taken in grams. This is also known as molar atomic mass.

Note...

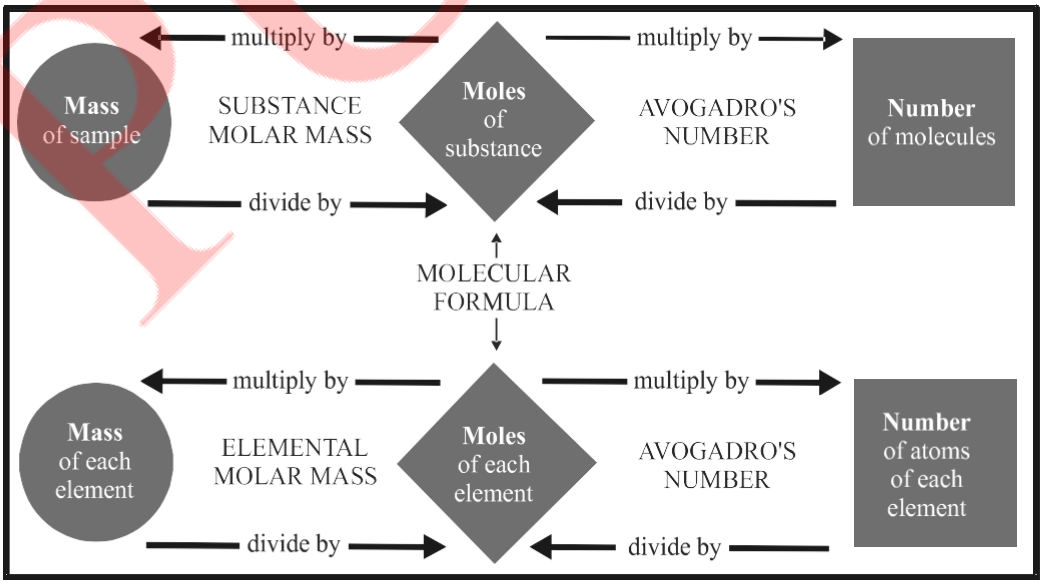
- Mass of 1 atom in amu and mass of 6.022×10^{23} atoms in grams are numerically equal.
- When atomic mass is taken in grams it is also called the molar atomic mass.
- 6.022×10^{23} is also called 1 mole of atoms and this number is also called the Avogadro's Number.
- Mole is just a number. As 1 dozen = 12;

  1 million = 10^6; 1 mole = 6.022×10^{23}.

10. MOLECULES

A group of similar or dissimilar atoms which exist together in nature is known as a molecule. e.g. H_2, NH_3.

The mass of molecules is measured by adding the masses of the atoms which constitute the molecule. Thus, the mass of a molecule can also be represented by the two methods used for measuring the mass of an atom viz. amu and g/mol.



11. CHEMICAL REACTIONS

A chemical reaction is only rearrangement of atoms. Atoms from different molecules (may be even same molecule) rearrange themselves to form new molecules.

Points to remember :

- ✦ Always balance chemical equations before doing any calculations
- ✦ The number of molecules in a reaction need not to be conserved e.g.

  $N_2 + 3\ H_2 \rightarrow 2\ NH_3$. The number of molecules is not conserved

  If we talk about only rearrangement of atoms in a balanced chemical reaction then it is evident that the mass of the atoms in the reactants side is equal to the sum of the masses of the atoms on the products side. This is the Law of Conservation of Atoms and Law of Conservation of Mass.

12. STOICHIOMETRY

The study of chemical reactions and calculations related to it is called Stoichiometry. The coefficients used to balance the reaction are called Stoichiometric Coefficients.

Points to remember :

- ✦ The stoichiometric coefficients give the ratio of molecules or moles that react and not the ratio of masses.
- ✦ Stoichiometric ratios can be used to predict the moles of product formed only if all the reactants are present in the stoichiometric ratios.

  Practically the amount of products formed is always less than the amount predicted by theoretical calculations

12.1 Limiting Reagent (LR) and Excess Reagent (ER)

If the reactants are not taken in the stoichiometric ratios then the reactant which is less than the required amount determines how much product will be formed and is known as the Limiting Reagent and the reactant present in excess is called the Excess Reagent. e.g. if we burn carbon in air (which has an infinite supply of oxygen) then the amount of CO_2 being produced will be governed by the amount of carbon taken. In this case, Carbon is the LR and O_2 is the ER.

13. PERCENT YIELD

As discussed earlier, due to practical reasons the amount of product formed by a chemical reaction is less than the amount predicted by theoretical calculations. The ratio of the amount of product formed to the amount predicted when multiplied by 100 gives the percentage yield.

$$\text{Percentage Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100$$

14. REACTIONS IN AQUEOUS MEDIA

Two solids cannot react with each other in solid phase and hence need to be dissolved in a liquid. When a solute is dissolved in a solvent, they co-exist in a single phase called the solution. Various parameters are used to measure the strength of a solution.

The strength of a solution denotes the amount of solute which is contained in the solution. The parameters used to denote the strength of a solution are:

- ✦ Mole fraction X : moles of a component / Total moles of solution.
- ✦ Mass% : Mass of solute (in g) present in 100g of solution.
- ✦ Mass/Vol : Mass of solute (in g) present in 100mL of solution
- ✦ v/v : Volume of solute/volume of solution {only for liq-liq solutions}
- ✦ g/L : Wt. of solute (g) in 1L of solution
- ✦ ppm: $\dfrac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$
- ✦ Molarity (M) : $\dfrac{\text{moles of solute}}{\text{volume of solution (L)}}$
- ✦ Molality (m) : $\dfrac{\text{moles of solute}}{\text{mass of solvent (kg)}}$

IMPORTANT RELATIONS

1. Relation between molality (m) Molarity (M), density (d) of solution and molar mass of solute (M_O)

   d : density in g/mL

   M_O: molar mass in g mol^{-1}

$$\text{Molality, } m = \frac{M \times 1000}{1000d - MM_O}$$

2. Relationship between molality (m) and mole fraction (X_B) of the solute

$$m = \frac{X_B}{1 - X_B} \times \frac{1000}{M_A} \qquad m = \frac{1 - X_A}{X_A} \times \frac{1000}{M_A}$$

Points to remember :

- ✦ Molarity is the most common unit of measuring strength of solution.
- ✦ The product of Molarity and Volume of the solution gives the number of moles of the solute, $n = M \times V$
- ✦ All the formulae of strength have amount of solute. (weight or moles) in the numerator.
- ✦ All the formulae have amount of solution in the denominator except for molality (m).

15. DILUTION LAW

When a solution is diluted, more solvent is added, the moles of solute remains unchanged. If the volume of a solution having a Molarity of M_1 is changed from V_1 to V_2 we can write that:

$$M_1V_1 = \text{moles of solute in the solution} = M_2V_2$$

16. EFFECT OF TEMPERATURE

Volume of the solvent increases on increasing the temperature. But it shows no effect on the mass of solute in the solution assuming the system to be closed i.e. no loss of mass.

The formulae of strength of solutions which do not involve volume of solution are unaffected by changes in temperature. e.g. molality remains unchanged with temperature. Formulae involving volume are altered by temperature e.g. Molarity.

17. INTRODUCTION TO EQUIVALENT CONCEPT

Equivalent concept is a way of understanding reactions and processes in chemistry which are often made simple by the use of Equivalent concept.

Equivalent Mass

"The mass of an acid which furnishes 1 mol H^+ is called its Equivalent mass."

"The mass of the base which furnishes 1 mol OH^- is called its Equivalent mass."

Valency Factor (Z)

Valency factor is the number of H^+ ions supplied by 1 molecule or mole of an acid or the number of OH^- ions supplied by 1 molecule or 1 mole of the base.

$$\text{Equivalent mass, } E = \frac{\text{Molecular Mass}}{Z}$$

Equivalents

$$\text{No. of equivalents} = \frac{\text{wt. of acid / base taken}}{\text{Eq. wt.}}$$

Note...

It should be always remembered that 1 equivalent of an acid reacts with 1 equivalent of a base.

18. MIXTURE OF ACIDS AND BASES

Whenever we have a mixture of multiple acids and bases we can find whether the resultant solution would be acidic or basic by using the equivalent concept. For a mixture of multiple acids and bases find out the equivalents of acids and bases taken and find which one of them is in excess.

19. LAW OF CHEMICAL EQUIVALENCE

According to this law, one equivalent of a reactant combines with one equivalent of the other reactant to give one equivalent of each product . For, example in a reaction $aA + bB \rightarrow cC + dD$ irrespective of the stoichiometric coefficients, 1 eq. of A reacts with 1 eq. of B to give 1 eq. each of C and 1eq of D

20. EQUIVALENT WEIGHTS OF SALTS

To calculate the equivalent weights of compounds which are neither acids nor bases, we need to know the charge on the cation or the anion. The mass of the cation divided by the charge on it is called the equivalent mass of the cation and the mass of the anion divided by the charge on it is called the equivalent mass of the anion. When we add the equivalent masses of the anion and the cation, it gives us the equivalent mass of the salt. For salts, Z in the total amount of positive or negative charge furnished by 1 mol of the salt.

21. ORIGIN OF EQUIVALENT CONCEPT

Equivalent weight of an element was initially defined as weight of an element which combines with 1g of hydrogen. Later the definition wad modified to : Equivalent weight of an element is that weight of the element which combines with 8g of Oxygen.

Note...

Same element can have multiple equivalent weights depending upon the charge on it. e.g. Fe^{2+} and Fe^{3+}.

22. EQUIVALENT VOLUME OF GASES

Equivalent volume of gas is the volume occupied by 1 equivalent of a gas at STP.

Equivalent mass of gas = molecular mass /Z.

Since 1 mole of gas occupies 22.4L at STP therefore 1 equivalent of a gas will occupy 22.4/Z L at STP. e.g. Oxygen occupies 5.6L, Chlorine and Hydrogen occupy 11.2L.

23. NORMALITY

The normality of a solution is the number of equivalents of solute present in 1L of the solution.

$$N = \frac{\text{equivalents of solute}}{\text{volume of solution (L)}}$$

The number of equivalents of solute present in a solution is given by Normality × Volume (L).

On dilution of the solution the number of equivalents of the solute is conserved and thus, we can apply the formula : $N_1V_1 = N_2V_2$

Caution :

Please note that the above equation gives rise to a lot of confusion and is a common mistake that students make. This is the equation of dilution where the number of equivalents are conserved. Now, since one equivalent of a reactant always reacts with 1 equivalent of another reactant a similar equation is used in problems involving titration of acids and bases. Please do not extend the same logic to molarity.

Relationship between Normality and Molarity

$N = M \times Z$; where 'Z' is the Valency factor

IMPORTANT INFORMATION

S.No.	Common Name	Chemical Name	Formulae
1.	Alum	Hydrated double sulphate of potassium and aluminium	$K_2SO_4.Al_2(SO_4)_3.24\,H_2O$
2.	Alumina	Aluminium oxide	Al_2O_3
3.	Ammonia water	Ammonium hydroxide	NH_4OH
4.	Angelsite	Lead sulphate	$PbSO_4$
5.	Aqua fortis	Concentrated nitric acid	HNO_3
6.	Aqua regia	....	$3HCl(Conc) + HNO_3(Conc)$
7.	Azote gas	Nitrogen	N_2
8.	Azurite blue	Basic copper carbonate	$2CuCO_3.Cu(OH)_2$
9.	Baking Soda	Sodium hydrogen carbonate	$NaHCO_3$
10.	Baryta	Barium Hydroxide	$Ba(OH)_2$
11.	Basic lead acetate	....	$Pb(OH)_2Pb(CH_3COO)_2$
12.	Bauxite	Dihydrate Aluminium oxide	$Al_2O_3.2H_2O$
13.	Blue Vitriol	Pentahydrate of cupric sulphate	$CuSO_4.5H_2O$
14.	Bleaching powder	Calcium oxychloride or calcium (hypochlorite) chloride	$CaOCl_2$ or $Ca(OCl)Cl$
15.	Borax	Sodium tetraborate	$Na_2B_4O_7.10H_2O$
16.	Brimstone	Sulphur	S
17.	Brine or common salt or rock salt	Sodium Chloride	$NaCl$
18.	Cerusite	Lead carbonate	$PbCO_3$
19.	Chalk or limestone	Calcium Carbonate	$CaCO_3$
20.	Chile saltpetre of Caliche	Sodium nitrate	$NaNO_3$
21.	Cuprite or ruby copper	Cuprous oxide	Cu_2O
22.	Copper glance	Copper sulphide	Cu_2S
23.	Carnalite	Potassium magnesium chloride	$KCl.MgCl_2.6H_2O$
24.	Calomel	Mercurous chloride	Hg_2Cl_2
25.	Cane sugar or Beet sugar	Sucrose	$C_{12}H_{22}O_{11}$
26.	Calgon	Sodium hexa-metaphosphate	$Na_2[Na_4(PO_3)_6]$
27.	Caustic soda	Sodium hydroxide	$NaOH$
28.	Caustic potash	Potassium hydroxide	KOH
29.	Calamine	Zinc carbonate	$ZnCO_3$
30.	Corundum	Aluminium oxide	Al_2O_3
31.	Dead burnt gypsum	Anhydrous calcium sulphate	$CaSO_4$
32.	Diaspore	Monohydrate aluminium oxide	$Al_2O_3.H_2O$
33.	Dry ice	Solid carbon dioxide	CO_2 (solid)
34.	Epsom salt	Heptahydrate of magnesium sulphate	$MgSO_4.7H_2O$
35.	Fluorspar	Calcium fluoride	CaF_2
36.	Galena	Lead sulphide	PbS
37.	Glauber's salt	Hydrated sodium sulphate	$Na_2SO_4.10H_2O$
38.	Green Vitriol	Ferrous sulphate	$FeSO_4.7H_2O$
39.	Gypsum	Calcium sulphate dihydrate	$CaSO_4.2H_2O$
40.	Hydrolith	Calcium hydride	CaH_2
41.	Hypo	Sodium thiosulphate	$Na_2S_2O_3.5H_2O$
42.	Iron pyrites	Iron disulphide	FeS_2
43.	Laughing gas	Dinitrogen oxide	N_2O
44.	Limonite	Hydrated ferric oxide	$Fe_2O_3.3H_2O$
45.	Litharge	Lead monoxide	PbO
46.	Lime	Calcium oxide	CaO

47.	Lime water or slaked lime	Calcium hydroxide	$Ca(OH)_2$
48.	Lime stone or chalk or marble	Calcium carbonate	$CaCO_3$
49.	Lunar caustic	Silver nitrate	$AgNO_3$
50.	Magnetite	Ferrosoferric oxide	Fe_3O_4
51.	Milk of lime	Calcium hydroxide	$Ca(OH)_2$
52.	Milk of magnesia	Magnesium hydroxide	$Mg(OH)_2$
53.	Marsh gas	Methane	CH_4
54.	Malachite (green)	Basic copper carbonate	$CuCO_3.Cu(OH)_2$
55.	Magnesia	Magnesium oxide	MgO
56.	Magnesite	Magnesium carbonate	$MgCO_3$
57.	Mohr's salt	Ferrous ammonium sulphate hexahydrate	$(NH_4)_2SO_4\ FeSO_4.6H_2O$
58.	Muriatic acid	Hydrochloric acid	HCl
59.	Nessler's reagent	Potassium tetra-idomercurate	$K_2[Hg\ I_4]$
60.	Nitre	Potassium nitrate	KNO_3
61.	Nitre cake	Sodium hydrogen sulphate	$NaHSO_4$
62.	Nitrolim	Calcium cyanamide plus carbon	$CaCN_2 + C$
63.	Nitrate of lime (Nitrolime)	Basic calcium nitrate	$Ca(NO_3)_2.CaO$
64.	Oil of Vitriol	Concentrated Sulphuric acid	H_2SO_4
65.	Oleum	Pyrosulphuric acid	$H_2S_2O_7$
66.	Pearl ash	Potassium carbonate	K_2CO_3
67.	Philosopher's wool	Zinc oxide	ZnO
68.	Phosgene	Carbonyl chloride	$COCl_2$
69.	Potash	Potassium carbonate	K_2CO_3
70.	Potash alum	Potassium aluminium sulphate	$K_2SO_4.Al_2(SO_4)_3.24H_2O$
71.	Plaster of Paris	Hemihydrate of calcium sulphate	$CaSO_4.\frac{1}{2}H_2O$
72.	Pyrogallol	Benzene-1, 2, 3-triol	$C_6H_3(OH)_3$
73.	Pyrolusite	Manganese dioxide	MnO_2
74.	Quartz or silica	Silicon dioxide	SiO_2
75.	Quick lime	Calcium oxide	CaO
76.	Quick silver	Mercury	Hg
77.	Red lead	Triplumbic tetroxide	Pb_3O_4
78.	Rock salt	Sodium chloride	$NaCl$
79.	Rough	Ferric oxide	Fe_2O_3
80.	Sal ammoniac	Solid ammonium chloride	NH_4Cl
81.	Sal volatile	Solid ammonium carbonate	$(NH_4)_2CO_3$
82.	Salt cake	Anhydrous sodium sulphate	Na_2SO_4
83.	Salt petre	Potassium nitrate	KNO_3
84.	Siderite	Ferrous carbonate	$FeCO_3$
85.	Silica	Silicon dioxide	SiO_2
86.	Silica gel	Hydrated silica	SiO_2, xH_2O
87.	Slaked lime	Calcium hydroxide	$Ca(OH)_2$
88.	Soda ash	Anhydrous sodium carbonate	Na_2CO_3
89.	Water glass	Sodium dioxide containing excess of silica	$Na_2SiO_3.SiO_2$
90.	Super phosphate of lime	Mixture of calcium dihydrogen phosphate and calcium sulphate	$Ca(H_2PO_4)_2.H_2O + 2CaSO_4.2H_2O$
91.	Verdigris	Basic copper acetate	$Cu(CH_3COO)_2$
92.	White lead	Basic lead carbonate	$2PbCO_3.Pb(OH)_2$
93.	White Vitriol	Heptahydrate of zinc sulphate	$ZnSO_4.7H_2O$
94.	Washing soda	Hydrated sodium carbonate	$Na_2CO_3.10H_2O$
95.	Zincite	Zinc oxide	ZnO
96.	Zinc blende	Zinc sulphide	ZnS

VALENCY OF SOME COMMON BASIC AND ACIDIC RADICALS

Electrovalent positive ions (basic radicals)

Monovalent

1.	Ammonium	NH_4^+
2.	Aurous [Gold (I)]	Au^+
3.	Cuprous [Copper (I)]	Cu^+
4.	Hydrogen	H^+
5.	Mercurous [Mercury (I)]	Hg^+
6.	Potassium	K^+
7.	Sodium	Na^+
8.	Argentous [Silver (I)]	Ag^+
9.	Lithium	Li^+

Divalent

1.	Argentic [Silver(II)]	Ag^{2+}
2.	Barium	Ba^{2+}
3.	Calcium	Ca^{2+}
4.	Cupric [Copper(II)]	Cu^{2+}
5.	Ferrous [Iron (II)]	Fe^{2+}
6.	Magnesium	Mg^{2+}
7.	Mercuric [Mercury (II)]	Hg^{2+}
8.	Plumbous [Lead (II)]	Pb^{2+}
9.	Stannous [Tin (II)]	Sn^{2+}
10.	Zinc	Zn^{2+}
11.	Platinous [Platinum (II)]	Pt^{2+}
12.	Nickel	Ni^{2+}

Trivalent

1.	Aluminium	Al^{3+}
2.	Ferric [Iron (III)]	Fe^{3+}
3.	Chromium	Cr^{3+}
4.	Auric [Gold (III)]	Au^{3+}
5.	Bismuth	Bi^{3+}
6.	Arsenic	As^{3+}

Tetravalent

1.	Plumbic [Lead (IV)]	Pb^{4+}
2.	Stannic [Tin (IV)]	Sn^{4+}
3.	Platinic [Platinium (IV)]	Pt^{4+}

ELECTROVALENT NEGATIVE IONS (ACIDIC RADICALS)

Monovalent

1.	Acetate	CH_3COO^-
2.	Bicarbonate or Hydrogen carbonate	HCO_3^-
3.	Bisulphide or Hydrogen sulphide	HS^-
4.	Bisulphate or Hydrogen sulphate	HSO_4^-
5.	Bisulphite or Hydrogen sulphite	HSO_3^-
6.	Bromide	Br^-
7.	Chloride	Cl^-
8.	Permanganate	MnO_4^-
9.	Fluoride	F^-
10.	Hydride	H^-
11.	Hydroxide	OH^-
12.	Iodide	I^-
13.	Cyanide	CN^-
14.	Nitrate	NO_3^-
15.	Nitrite	NO_2^-
16.	Chlorite	ClO_2^-
17.	Hypochlorite	ClO^-
18.	Chlorate	ClO_3^-
19.	Perchlorate	ClO_4^-
20.	Meta aluminate	AlO_2^-

Divalent

1.	Carbonate	CO_3^{2-}
2.	Dichromate	$Cr_2O_7^{2-}$
3.	Oxide	O^{2-}
4.	Peroxide	O_2^{2-}
5.	Sulphate	SO_4^{2-}
6.	Sulphite	SO_3^{2-}
7.	Sulphide	S^{2-}
8.	Silicate	SiO_3^{2-}
9.	Thiosulphate	$S_2O_3^{2-}$
10.	Zincate	ZnO_2^{2-}
11.	Plumbite	PbO_2^{2-}
12.	Stannate	SnO_3^{2-}
13.	Manganate	MnO_4^{2-}
14.	Chromate	CrO_4^{2-}
15.	Oxalate	$(COO)_2^{2-}$

Trivalent

1.	Arsenate	AsO_4^{3-}
2.	Nitride	N^{3-}
3.	Arsenite	AsO_3^{3-}
4.	Phosphide	P^{3-}
5.	Phosphite	PO_3^{3-}
6.	Phosphate	PO_4^{3-}
7.	Borate	BO_3^{3-}
8.	Aluminate	AlO_3^{3-}

Tetravalent

1.	Carbide	C^{4-}
2.	Ferrocyanide	$Fe(CN)_6^{4-}$

STRUCTURE OF ATOM

1. INTRODUCTION

In this chapter, we explore the inside world of atoms which is full of mystery and surprises. Whole chemistry is based on atoms and their structures. We will also study the behaviour exhibited by the electrons and their consequences.

1.1 Discovery of fundamental particles

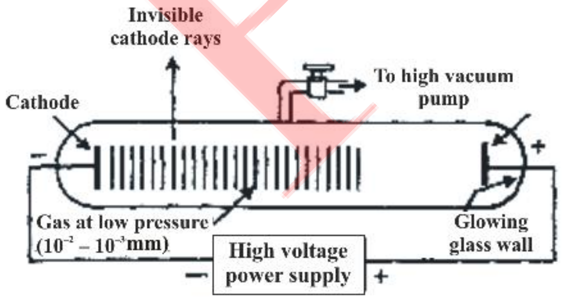
Dalton's atomic theory was able to explain the law of conservation of mass, law of constant composition and law of multiple proportion very successfully but it failed to explain the results of many experiments like it was known that substances like glass or ebonite when rubbed with silk or fur generate electricity

1.1.1 Discovery of electron

William Crookes in 1879 studied the electrical discharge in partially evacuated tubes known as **cathode ray discharge tubes.**

A discharge tube is made of glass, about 60cm long containing two thin pieces of metals called electrodes, sealed in it. This is known as crooke's tube. The negative electrode is known as **cathode** and positive electrode is known **anode.**

When a gas enclosed at low pressure(~ 10^{-4} atm) in discharge tube is subjected to a high voltage (~ 10,000V), invisible rays originating from the cathode and producing a greenish glow behind the perforated anode on the glass wall coated with phosphorescent material ZnS is observed. These rays were called **cathode rays.**

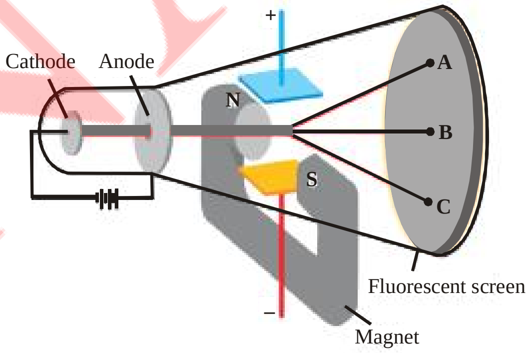


1.1.2 Properties

1. They produce sharp shadow of the solid object in their path suggesting that they travel in straight line.
2. They are deflected towards the positive plate in an electric field suggesting that they are negatively charged. They were named as electrons by Stoney.
3. They can make a light paddle wheel to rotate placed in their path. This means they possess kinetic energy and are material particles.
4. They have a charge to mass ratio = 1.75882 × 10^{11}C/kg
5. They ionise gases through which they travel.
6. They produce X-rays when they strike a metallic target.
7. The characterstics of cathode rays (electrons) do not depend on the material of electrodes and nature of the gas present in the cathode ray tube.

Thus, we can conclude that electrons are basic constituents of all matter.

1.1.3 Charge to mass ratio of electron

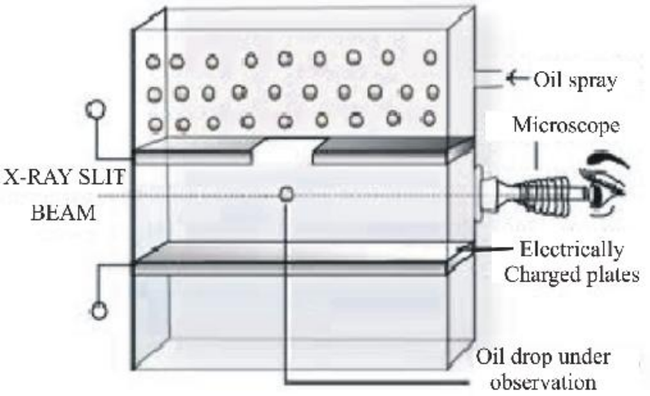


In 1897 J.J. Thomson measured e/m ratio of electron by using cathode ray tube and applying electric and magnetic field perpendicular to each other as well as to the path of electrons. The extent of deviation of electrons from their path in the presence of electric and magnetic field depends on:

(a) Charge on the electron
(b) Mass of the particle
(c) The strength of electric or magnetic field

When only electric field is applied, the electrons are deflected to the point A. When only magnetic field is applied the electrons are deflected to the point C. By balancing the strengths of electric or magnetic fields, the electrons are allowed to hit the screen at point B i.e. the point where electrons hit in the absence of electric and magnetic field. By measuring the amount of deflections Thomson was able to calculate the value of e/m as 1.758820 × 10^{11}C/kg.

1.1.4 Charge on the electron



R.A Millikan devised a method known as oil drop experiment to determine the charge on the electrons.

In this method, oil droplets in the form of mist, produced by the atomiser, were allowed to enter through a tiny hole in the upper plate of electrical condenser. The downward motion of these droplets was viewed through the telescope, equipped with a micrometer eye piece. By measuring the rate of fall of these droplets, Millikan was able to measure the mass of oil droplets. The air inside the chamber was ionized by passing a beam of X-rays through it. The electrical charge on these oil droplets was acquired by collisions with gaseous ions. The fall of these charged oil droplets can be retarded, accelerated or made stationary depending upon the charge on the droplets and the polarity and strength of the voltage applied to the plate. By carefully measuring the effects of electrical field strength on the motion of oil droplets, Millikan concluded that the magnitude of electrical charge, q, on the droplets is always an integral multiple of the electrical charge e, that is, $q = n\,e$, where n = 1, 2, 3... .

Charge on the electron is found to be -1.6022×10^{-19}C.

The mass of electron was thus calculated as

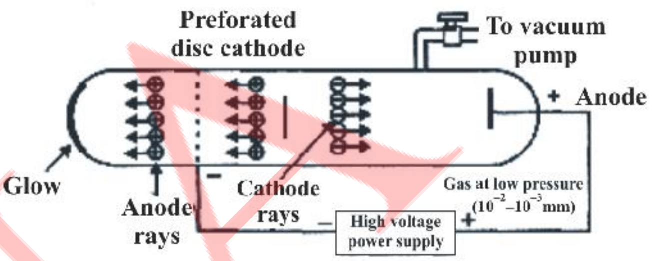
$$m = \frac{e}{e/m} = \frac{1.6022\times10^{-19}\,\text{C}}{1.758820\times10^{11}\,\text{C/kg}} = 9.1094\times10^{-31}\,\text{kg}.$$

1.1.5 Origin of cathode rays

The cathode rays are first produced from the material of the cathode and then from the gas inside the discharge tube due to bombardment of the gas molecules by the high speed electrons emitted first from the cathode.

1.2.1 Discovery of proton

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. So, during the experiments with cathode rays, the scientist Goldstein designed a special type of discharge tube. He discovered new rays called **Canal rays.** The name canal rays is derived from the fact that the rays travelled in straight line through a vacuum tube in the opposite direction to cathode rays, pass through and emerge from a canal or hole in the cathode. They are also known as **anode rays.**



1.2.2 Properties:

1. They travel in straight lines.
2. They carry a positive charge.
3. They are made up of material particles.
4. The value of the charge on the particles constituting the anode rays is found to depend on the nature of gas taken.
5. The mass of the particles constituting the anode rays is found to depend on the nature of gas taken.
6. The charge to mass ratio(e/m) of the particles is also found to depend on the gas taken.
7. Their behaviour in electric and magnetic field is opposite to that observed for electron.

1.2.3 Origin of anode rays:

These rays are believed to be produced as a result of the knock out of the electrons from the gaseous atoms by the bombardment of high speed electrons of the cathode rays on them. These anode rays are not emitted from the anode but are produced in the space between the anode and the cathode.

The lightest charged particles were obtained when the gas taken in the discharge tube was hydrogen. The e/m value of these particles were maximum. They had minimum mass and unit positive charge. The particle was called a proton.

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

Mass of a proton = 1.672×10^{-27}kg

1.3.1 Discovery of neutron

The theoretical requirement for the existence of a neutron particle in the atomic nucleus was put forward by Rutherford in 1920.It was proposed to be a particle with no charge and having mass almost equal to that of a proton. He named it as neutron. In 1932 Chadwick proved its existence. He observed that, when a beam of α particles $({}_4^2\text{He})$ is incident on Beryllium (Be), a new type of particle was ejected. It had mass almost equal to that of a **proton** (1.674×10^{-27}kg) and carried no charge.

$${}_5^{11}\text{B} + {}_2^4\text{He} \rightarrow {}_7^{14}\text{N} + {}_0^1\text{n}$$

$${}_4^9\text{Be} + {}_2^4\text{He} \rightarrow {}_6^{12}\text{C} + {}_0^1\text{n}$$

SUMMARY :

ATOMIC BUILDING BLOCKS

Name	Discoverer	Symbol	Charge	Relative Charge	Mass
Electron	J.J. Thomson	e	-1.6022×10^{-19} C	–1	9.1094×10^{-31} Kg
Proton	Goldstein	p	$+1.6022 \times 10^{-19}$C	+1	1.6726×10^{-27} kg
Neutron	Chadwick	n	0	0	1.6749×10^{-27} kg

2. DEFINATIONS

2.1 Electron

A fundamental particle which carries one unit negative charge and has a mass nearly equal to 1/1837th of that of hydrogen atom.

2.2 Proton

A fundamental particle which carries one unit positive charge and has a mass nearly equal to that of hydrogen atom.

2.3 Neutron

A fundamental particle which carries no charge but has a mass nearly equal to that of hydrogen atom.

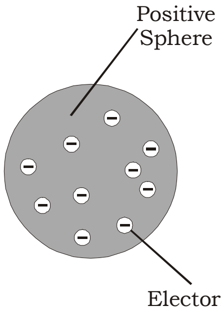
3. THOMSON MODEL

Sir J. J. Thomson, who discovered the electron, was the first to suggest a model of atomic structure.

(i) All atoms contain electrons.

(ii) The atom as a whole is neutral. The total positive charge and total negative charge must be equal.

He visualised all the positive charge of the atom as being spread out uniformly throughout a sphere of atomic dimensions (i.e. approx. 10^{-10} m in diameter). The electrons were smaller particles together carrying a negative charge, equal to the positive charge in the atom. They were studded in the atom like plums in a pudding. The charge distribution was such, that it gave the most stable arrangement. This model of the atom was often called the plum – pudding model. Also the raisin pudding model or watermelon model.



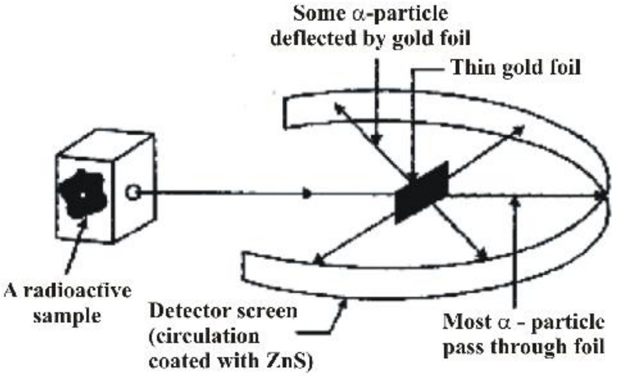
Thomson's proposed model of atom.

3.1 Drawbacks

Though the 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.

4. RUTHERFORD'S ~-SCATTERING EXPERIMENT

Rutherford conducted α- particles scattering experiments in 1909. In this experiment, a very thin foil of gold (0.004nm) is bombarded by a fine stream of alpha particles. A fluorescent screen (ZnS) is placed behind the gold foil, where points were recorded which were emerging from α-particles. Polonium was used as the source of α-particles.



RUTHERFORD'S SCATTERING EXPERIMENT

4.1 Observations

Rutherford carried out a number of experiments, involving the scattering of α – particles by a very thin foil of gold. Observations were:

(i) Most of the α – particles (99%) passes through it, without any deviation or deflection.

(ii) Some of the α – particles were deflected through small angles.

(iii) Very few α – particles were deflected by large angles and occasionally an α – particle got deflected by 180°

4.2 Conclusions

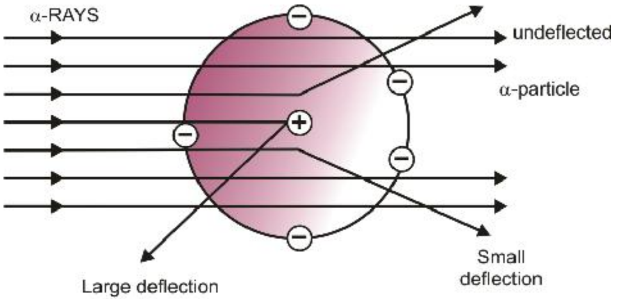
(i) An atom must be extremely hollow and must consist of mostly empty space because most of the particles passed through it without any deflection.

(ii) Very few particles were deflected to a large extent. This indicates that:

(a) Electrons because of their negative charge and very low mass cannot deflect heavy and positively charged α particles

(b) There must be a very heavy and positively charged body in the atom i.e. nucleus which does not permit the passage of positively charged α particles.

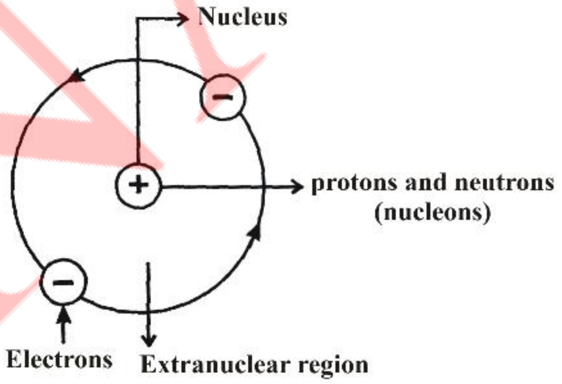
(c) Because, the number of α particles which undergo deflection of 180°, is very small, therefore the volume of positively charged body must be extremely small fraction of the total volume of the atom. This positively charged body must be at the centre of the atom which is called **nucleus.**



It has been found that radius of atom is of the order of 10^{-10}m while the radius of the nucleus is of the order of 10^{-15}m.

Thus if a cricket ball represents a nucleus, then the radius of atom would be about 5 km.

4.3 Rutherford's nuclear atomic model



(i) An atom consists of tiny positively charged nucleus at the centre and it is surrounded by hollow portion called extra nuclear part.

(ii) The positive charge of the nucleus is due to **nucleons** which consist of protons and neutrons while the electrons, present in extra nuclear portion has negligible mass and carry a negative charge.

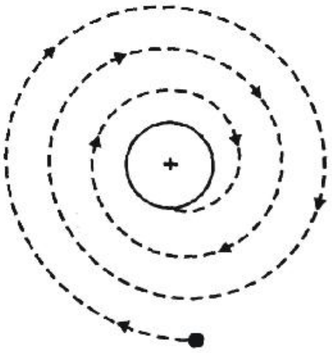
(iii) The atom is electrically neutral, as the number of electrons is equal to number of protons in it. Thus, total positive charge of the nucleus is balanced by the total negative charge of electrons.

(iv) The electrons in the extra nuclear part are revolving around the nucleus in circular paths called **orbits.** Thus, an atom resembles the solar system in which the sun plays the role of nucleus and the planets that of revolving electrons and the model is known as **planetary model.**

(v) Electrons and nucleus are held together by the electrostatic force of attraction.

(vi) Forces of attraction operating on the electron are exactly balanced by centrifugal forces.

4.4 Drawbacks



ELECTRON FALLING
INTO THE NUCLEUS

(i) According to classical mechanics, any charged body in motion under the influence of attractive forces should radiate energy continuously. If this is so, the electron will follow a spiral path and finally fall into the nucleus and the structure would collapse. This behaviour is never observed.

(ii) It says nothing about the electronic structure of atoms i.e. how the electrons are distributed around the nucleus and what are the energies of these electrons.

5. ATOMIC NUMBER AND MASS NUMBER

5.1 Atomic number (Z)

Atomic number of an element is equal to the number of unit positive charges or number of protons present in the nucleus of the atom of the element. It also represents the number of electrons in the neutral atom. Eg. Number of protons in Na = 11 , thus atomic number of Na=11

5.2 Mass number (A)

The elementary particles (protons and neutrons) present in the nucleus of an atom are collectively known as nucleons.

The mass number (A) of an atom is equal to the sum of protons and neutrons. It is always a whole number. Thus,

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

Therefore, **number of neutrons (n) = Mass Number (A) – Number of protons (Z)**

n = A – Z

Note..

The general notation that is used to represent the mass number and atomic number of a given atoms is ${}^{A}_{Z}X$

Where, X – symbol of element

A – Mass number

Z – atomic number

5.3 Isotopes, Isobars, isotones and Isoelectronic

5.3.1 Isotopes:

Isotopes are the atoms of the same element having identical atomic number but different mass number. The difference is due to the difference in number of neutrons.

The chemical properties of atoms are controlled by the number of electrons. Thus, isotopes of an element show same chemical behaviour.

Isotopes of Hydrogen

Isotope	Formula	Mass number	No. of protons	No. of neutrons
Protium	${}^{1}_{1}H$ (H)	1	1	0
Deuterium	${}^{2}_{1}H$ (D)	2	1	1
Tritium	${}^{3}_{1}H$ (T)	3	1	2

Isotopes of Oxygen

Isotope number	Mass number	No. of protons	No. of neutrons
${}^{16}_{8}O$	16	8	8
${}^{17}_{8}O$	17	8	9
${}^{18}_{8}O$	18	8	10

Isotopes of some common elements

Element	Isotopes
Carbon (C)	$^{12}_{6}C$, $^{13}_{6}C$, $^{14}_{6}C$
Nitrogen (N)	$^{14}_{7}N$, $^{15}_{7}N$
Uranium	$^{233}_{92}U$, $^{235}_{92}U$, $^{238}_{92}U$
Sulphur	$^{32}_{16}S$, $^{33}_{16}S$, $^{34}_{16}S$, $^{36}_{16}S$

5.3.2 Relative Abundance:

Isotopes of an element occur in different percentages in nature, which is termed as relative abundance.

Using this relative abundance the average atomic mass of the element can be calculated. For Example,

the average atomic mass of Cl is 35.5 due to existence of two isotopes ^{35}Cl and ^{37}Cl in 75% and 25% abundance respectively

5.3.3 Isobars:

Atoms of different elements having different atomic numbers but same mass numbers are called isobars. Eg

Isobar	Atomic number	Mass number	No. of elctrons	No. of protons	No. of neutrons
$^{40}_{18}Ar$	18	40	18	18	22
$^{40}_{19}K$	19	40	19	19	21
$^{40}_{20}Ca$	20	40	20	20	20

5.3.4 Isotones:

Atoms of different elements which contain the same number of neutrons are called isotones. Eg

Isotones	Atomic	Mass number	No. of neutros
$^{36}_{16}S$	16	36	20
$^{37}_{17}Cl$	17	37	20
$^{38}_{18}Ar$	18	38	20
$^{39}_{19}K$	19	39	20
$^{40}_{20}Ca$	20	40	20

5.3.5 Isoelectronic:

The species (atoms or ions) containing the same number of electrons are called isoelectronic. Eg.

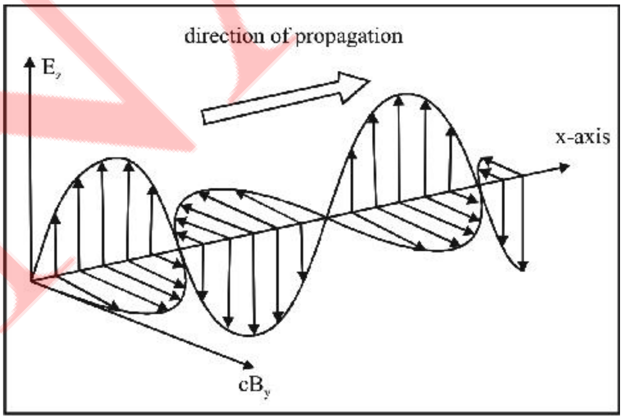
O^{2-}, F^{-}, Na^{+}, Mg^{+2}, Al^{+3}, Ne etc

To go further into the atomic mysteries, we will have to understand the nature of electromagnetic radiations and study **Maxwell's Electromagnetic Wave theory".**

James Maxwell was the first to give a comprehensive explanation about the interaction between the charged bodies and the behaviour of electric and magnetic fields.

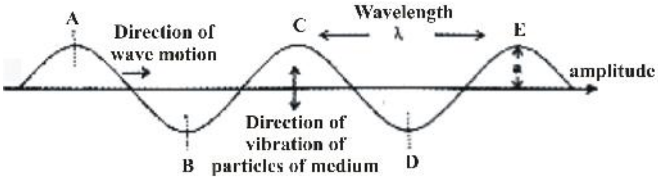
6. ELECTROMAGNETIC RADIATIONS

Electromagnetic Radiations are waves which are formed as a result of oscillating magnetic and electric fields which are perpendicular to each other and both are perpendicular to direction of motion.



They do not require any medium and can move in vacuum unlike sound waves.

Light is a form of radiation and has wave characterstics. The various characterstics of a wave are:



PROPAGATION OF A WAVE

1) **Amplitude :** It is height of the crest or trough (depth) of a wave. Units : metre (m)

2) **Frequency (¬) :** The number of waves passing through a point in one second. **Units :** Hertz (Hz) or s^{-1}

3) **Time Period :** The time taken by a wave to complete one vibration is called time period. **Units :** sec

4) **Velocity :** The distance travelled by a wave in one second is called velocity. **Units :** m/s

In vacuum, all types of electromagnetic radiations travel at the same speed i.e. **3×10^8 m/s.** This is called speed of light.

5) **Wavelength(ª) :** The distance between two adjacent crests or troughs is called wavelength. **Units :** Angstrom(Å)

[1 Å=10^{-10}m]

6) **Wave Number** ($\bar{\nu}$) **:** It is the number of wavelengths per centimetre of length. **Units :** m^{-1}

$$\bar{\nu} = 1/\lambda$$

6.1 Relationship between velocity, frequency & wavelength

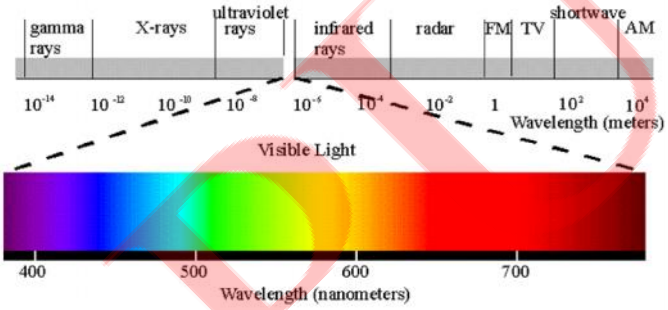
$$c = \nu\lambda$$

where **c :** speed of light i.e. 3×10^8 m/s in vaccum

v : frequency; ª**:** wavelength

7. ELECTROMAGNETIC SPECTRUM

When all the electromagnetic radiations are arranged in increasing order of wavelength or decreasing frequency the band of radiations obtained is termed as electromagnetic spectrum.



The visible spectrum is a subset of this spectrum (VIBGYOR) whose range of wavelength is 380-760nm.

The wavelengths increase in the order:

Gamma Rays < X-rays < Ultra-violet rays < Visible< Infrared < Micro-waves <Radio waves.

7.1 Electromagnetic Wave Theory

The main points of this theory are:

(1) A source (like the heated rod) emits energy **continuously** in the form of radiations (i.e. no change in wavelength or frequency of the emitted radiations even on increasing the energy radiated).

(2) These radiations are Electromagnetic in nature.

7.2 Failure of EM wave theory

The theory failed because of 2 experiments:

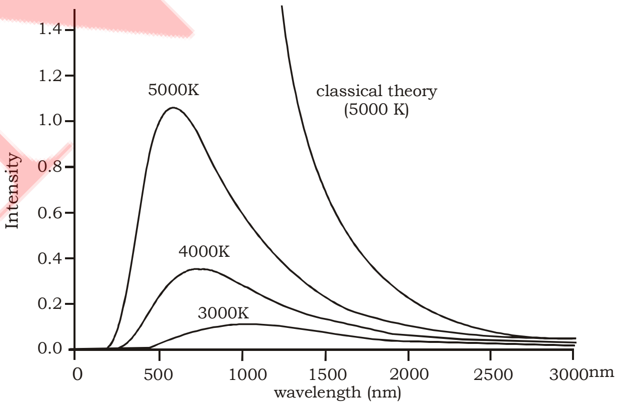
(1) **Black Body Radiation :**

According to Maxwell's theory on heating a body the intensity should increase, that is, energy radiated per unit area should increase without having any effect on the wavelength or frequency.

But we observe that when we heat an iron rod, it first turns to red then white and then becomes blue at very high temperatures. This means that frequency of emitted radiations is changing.

An ideal body, which emits and absorbs radiations of all frequencies is called **black body** and radiation emitted by a black body is called **black body radiation**

The variation of intensity with wavelength at different temperatures for a black body is shown below:

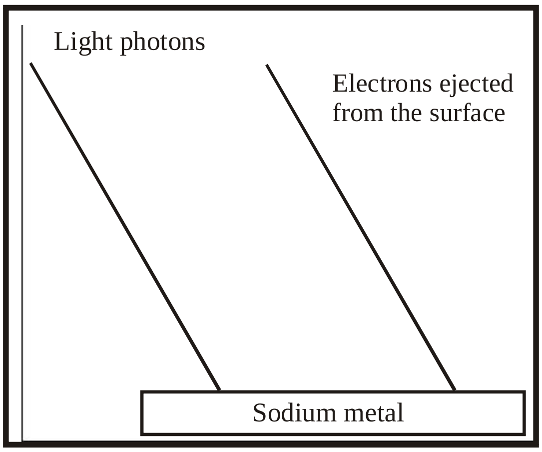


So it is observed that with increasing temperature the dominant wavelength in the emitted radiations decreases and the frequency increases.

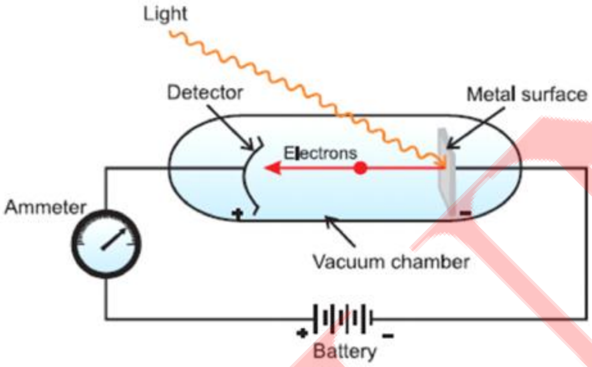
That is at higher temperatures, though the intensity rises as predicted by Maxwell's theory but the wavelength decreases. If **T_1>T_2>T_3 then** ª$_1$< ª$_2$< ª$_3$.

(2) **Photoelectric Effect**

When radiations with certain minimum frequency (ν_0) strike the surface of a metal, the electrons are ejected from the surface of the metal. This phenomena is called **photoelectric effect.** The electrons emitted are called **photoelectrons.**



According to Maxwell's Theory the ejection of electrons should depend on intensity of radiation that is if electrons are not being ejected, then on increasing the intensity they can be ejected.



The following **observations** are made:

(i) The electrons are ejected from the metal surface as soon as the beam of light strikes the surface, i.e., there is no time lag between the striking of light beam and the ejection of electrons from the metal surface.

(ii) The number of electrons ejected is proportional to the intensity or brightness of light.

(iii) For each metal, there is a characteristic minimum frequency, ν_0 (also known as **threshold frequency**) below which photoelectric effect is not observed. At a frequency $\nu > \nu_0$, the ejected electrons come out with certain kinetic energy. The kinetic energies of these electrons increase with the increase of frequency of the light used.

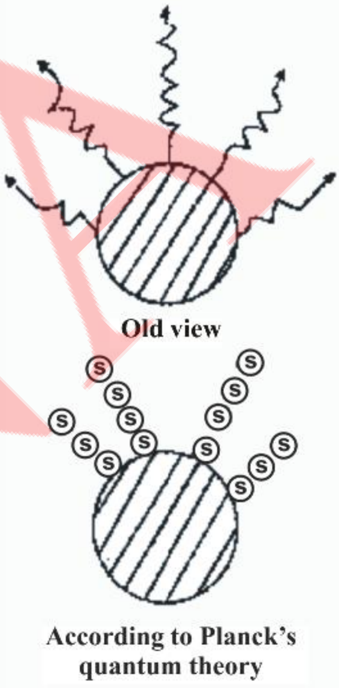
Thus, these findings were contradictory to the Maxwell's theory. The number of electrons ejected and kinetic energy associated with them should depend on the intensity of light. It has been observed that though the number of electrons ejected does depend upon the brightness of light, the kinetic energy of the ejected electrons does not.

To justify these findings Max Von Planc gave his Quantum theory.

8. PLANCK'S QUANTUM THEORY

The main points of this theory are:

(i) The 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 a **'quantum'.** In case of light this quantum of energy is called a **photon.**



(ii) At a time only one photon can be supplied to one electron or any other particle.

(iii) One quantum cannot be divided or distributed.

(iv) The energy of each quantum is directly proportional to the frequency of radiation.

$$E \propto \nu \text{ or } E = h\nu = \frac{hc}{\lambda}$$

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

(v) The total energy emitted or absorbed by a body will be in whole number quanta.

Hence $$\mathbf{E} = nh\nu = \frac{nhc}{\lambda}$$

This is also called **"Quantisation of energy".**

8.1 Explanation of Black body radiation

As the temperature is increased the energy emitted increases thereby increasing the frequency of the emitted radiations. As the frequency increases the wavelength shifts to lower values.

8.2 Explanation of Photoelectric effect

(i) 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 ejected from the metal only if the energy of the photon is sufficient to overcome the force of attraction of the electron by the nucleus. So, photoelectrons are ejected only when the incident light has a certain minimum frequency (threshold frequency ν_0). The Threshold energy required for emission is called **"Work Function"** that is **"$h\nu_0$".**

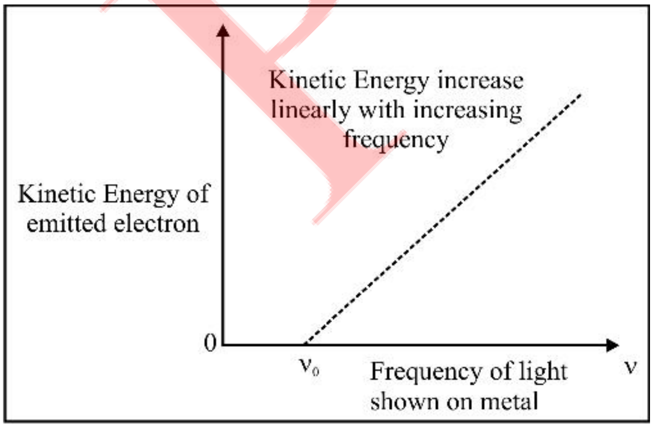
(ii) If the frequency of the incident light (ν) is more than the threshold frequency (ν_0), the excess energy is imparted to the electron as kinetic energy. Hence,

Energy of one quantum = Threshold Energy + Kinetic Energy

$$h\nu = h\nu_0 + (1/2)\, m_e v^2$$

(iii) When $\nu > \nu_0$, then on increasing the intensity the number of quanta incident increases thereby increasing the number of photoelectrons ejected.

(iv) When $\nu > \nu_0$, then on further increasing the frequency, the energy of each photon increases and thus kinetic energy of each ejected electron increases.



Note..

Energy can also be expressed in Electron Volt(eV).

The energy acquired by an electron when it is accelerated through a potential difference of one Volt.

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

CONCLUSION :

Light has both the **Wave nature** (shows the phenomena of diffraction and interference) **and Particle nature** (could explain the black body radiation and photoelectric effect) . Thus, light has dual nature.

Bohr's Model is based on "Atomic Spectra", therefore before moving further we will study:

9. WHAT IS SPECTRUM?

A spectrum is a group or band of wavelengths/colours and the study of emission or absorption spectra is known as spectroscopy.

9.1 Types of spectrum

There are two types of spectrum:

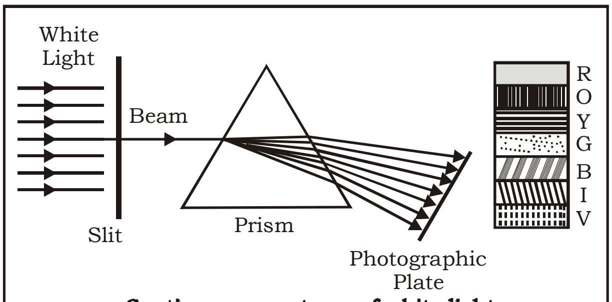
1) Emission Spectrum
2) Absorption Spectrum

9.2 Emission Spectrum

When radiations emitted from a source are incident on a prism and are separated into different wavelengths and obtained on a photographic plate.

(a) Continuous Emission Spectra:

There are no gaps between various wavelengths, one wavelength merges into another.

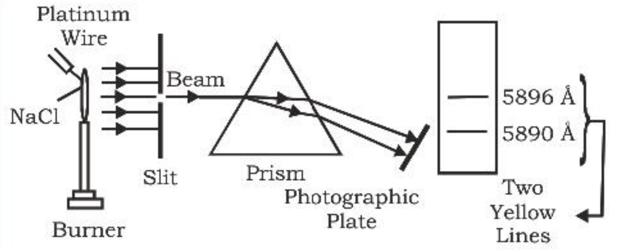


Continuous spectrum of white light

(b) **Discontinuous Emission Spectra:**

It is also known as **Line Spectra** or **atomic spectra.**

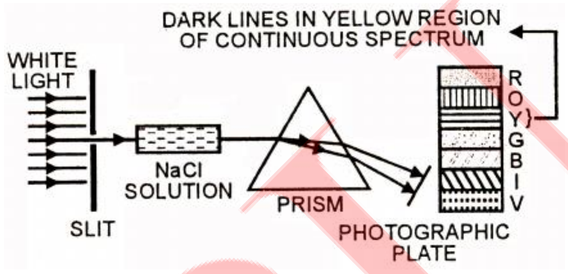
In this, certain wavelengths go missing from a group and that leaves dark spaces in between giving discontinuity to the spectrum. It is also known **as fingerprint of an element.**



Line Spectrum produced from a volatile salt placed in a flame.

9.3 Absorption Spectra

When light from any source is first passed through the solution of a chemical substance and then analysed, it is observed that there are some dark lines in the otherwise continuous spectra.



Production of absorption spectrum

Bohr studied the atomic spectra of hydrogen and based on that he proposed his model.

10. BOHR'S MODEL

Note: This model is applicable to H-atom or H-like species like He^{+},Li^{2+},Be^{3+}.

10.1 Postulates

1) An atom consists of a small, heavy, positively charged nucleus in the centre and the electrons revolve around it in circular orbits.

2) Electrons revolve only in those orbits which have a fixed value of energy. Hence, these orbits are called energy levels or stationary states.

They are numbered as 1,2,3,...... These numbers are known as **Principal quantum Numbers**.

(a) **Energy** of an electron is given by:

$E_n = -R_H(Z^2/n^2)$ n = 1,2,3.......

where R_H is Rydberg's constant and its value is 2.18×10^{-18} J.

Z = atomic number

$$E_n = -2.18\times10^{-18}\frac{Z^2}{n^2}\,J/atom$$

$$E_n = -13.6\frac{Z^2}{n^2}\,eV/atom$$

$$E_n = -1312\frac{Z^2}{n^2}\,kJ/mol$$

Thus, energies of various levels are in the order:

K < L < M < N...... and so on.

Energy of the lowest state(n=1) is called **ground state.**

(b) **Radii** of the stationary states:

$$r_n = \frac{52.9n^2}{Z}\,pm$$

For H-atom (Z = 1), the radius of first stationary state is called **Bohr orbit** (52.9 pm)

(c) **Velocities** of the electron in different orbits:

$$v_n = \frac{2.188\times10^6 Z}{n}\,m/s$$

3) Since the electrons revolve only in those orbits which have fixed values of energy, hence electrons in an atom can have only certain definite values of energy and not any of their own. Thus, **energy of an electron is quantised.**

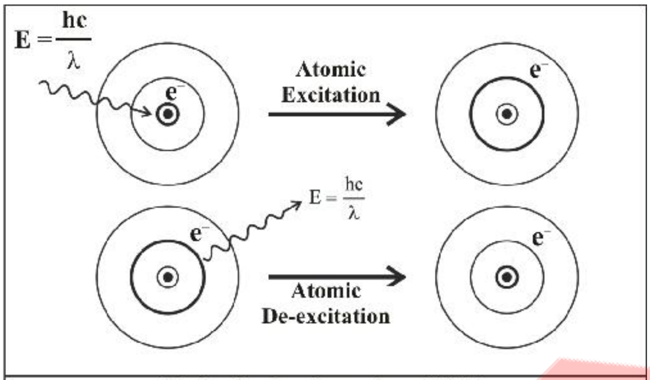
4) Like energy, the angular momentum of an electron in an atom can have certain definite values and not any value of their own.

$$mvr = \frac{nh}{2\pi}$$

Where n=1,2,3...... and so on.

5) An electron does not lose or gain energy when it is present in the same shell.

6) When an electron gains energy, it gets excited to higher energy levels and when it de-excites, it loses energy in the form of electromagnetic radiations and comes to lower energy values.



Excitation by absorption of light and de-excitation by emission of light

10.2 What does negative energy for Hydrogen atom means?

This negative sign means that the energy of the electron in the atom is lower than the energy of a free electron at rest. A free electron at rest is an electron that is infinitely far away from the nucleus $(n = \infty)$ and is assigned the energy value of zero. As the electron gets closer to the nucleus (as *n* decreases), *En* becomes more and more negative. The most negative energy value is given by *n*=1 which corresponds to the most stable orbit.

10.3 Transition of Electron

We know that energy is absorbed or emitted when electron excites or de-excites respectively. The energy gap between the two orbits is

$$\Delta E = E_f - E_i$$

$$\Delta E = \left(-\frac{R_H}{n_f^2}\right) - \left(-\frac{R_H}{n_i^2}\right)$$

$$\Delta E = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = 2.18\times10^{-18}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) J/atom$$

The wavelength associated with the absorption or emission of the photon is:

$$\frac{1}{\lambda} = \frac{\Delta E}{hc} = \frac{R_H}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = 1.09677\times10^{7}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) m^{-1}$$

This is known as Rydberg's formula.

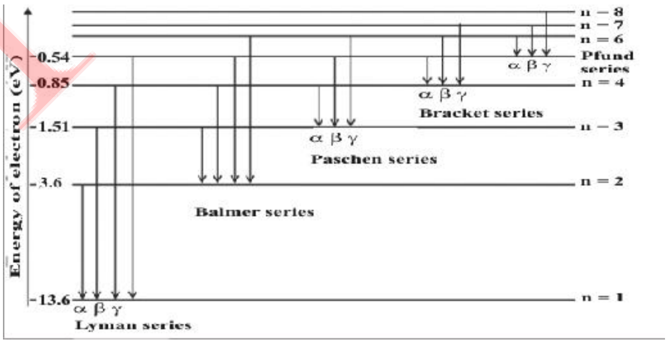
Note..

$1.09677 \times 10^7\ m^{-1}$ is also known as Rydberg's constant.

10.4 Line Spectrum of Hydrogen

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiations of discrete frequency. The hydrogen spectra consists of several lines named after their discoverer.

We get discrete lines and not a continuous spectra because the energy of an electron cannot change continuously but can have only definite values. Thus we can say that energy of an electron is quantised.



LYMAN SERIES :

When an electron jumps from any of the higher states to the ground state or first state (n = 1) ,the series of spectral lines emitted lies in the **ultra violet** region and are called as Lyman series.

Therefore , in Rydberg's formula $n_1 = 1$, $n_2 = 2,3,4,5...$

BALMER SERIES :

When an electron jumps from any of the higher states to the state with n=2,the series of spectral lines emitted lies in the **visible** region and are called as Balmer series.

Therefore , in Rydberg's formula $n_1 = 2$, $n_2 = 3,4,5,6....$

PASCHEN SERIES :

When an electron jumps from any of the higher states to the state with n=3 ,the series of spectral lines emitted lies in the **infrared** region and are called as Paschen series.

Therefore , in Rydberg's formula $n_1 = 3$, $n_2 = 4,5,6...$

BRACKETT SERIES :

When an electron jumps from any of the higher states to the state with n = 4,the series of spectral lines emitted lies in the **infrared** region and are called as Brackett series.

Therefore , in Rydberg's formula $n_1 = 4$, $n_2 = 5,6,7...$

PFUND SERIES :

When an electron jumps from any of the higher states to the state with n = 4,the series of spectral lines emitted lies in the **infrared** region and are called as Pfund series.

Therefore , in Rydberg's formula $n_1 = 5$, $n_2 = 6,7...$

10.5 Ionisation Energy

It is the energy required to remove the electron completely from the atom so as to convert it into a positive ion.

Thus, $n_1 = 1$ and $n_2 = \infty$

10.6 Limiting Line

It is the line of shortest wavelength i.e. $n_2 = \infty$

Note..

Although a hydrogen atom has only one electron, yet its spectra contains large number of lines. This is because a sample of hydrogen gas contains large number of molecules. When such a sample is heated to a high temperature, the hydrogen molecules split into hydrogen atoms. The electrons in different hydrogen atoms absorb different amounts of energies and are excited to different levels. When these electrons return, different electrons adopt different routes to return to the ground state. Thus, they emit different amounts of energies and thus large number of lines in atomic spectra in hydrogen.

Maximum no. of lines that can be emitted when an electron in an excited state n_2 de-excites to n_1 ($n_2 > n_1$) :

$$\frac{(n_2 - n_1 + 1)(n_2 - n_1)}{2}$$

10.7 Limitations of Bohr's Model

1) Inability to explain line spectra of multi-electron atoms.
2) It fails to account for the finer details (doublet-two closely spaced lines) of the hydrogen spectra.
3) Inability to explain splitting of lines in the magnetic field (Zeeman Effect) and in the electric field (Stark Effect)- If the source emitting the radiation is placed in magnetic or electric field, it is observed that each spectral line splits up into a number of lines. Splitting of spectral lines in magnetic field is known as Zeeman Effect while splitting of spectral lines in electric field is known as Stark Effect.
4) It could not explain the ability of atoms to form molecules by covalent bonds.
5) He ignores dual behaviour of matter and also contradicts Heisenberg uncertainty principle.

11. TOWARDS QUANTUM MECHANICAL MODEL

This model was based on two concepts:

(1) de Broglie Concept of dual nature of matter

(2) Heisenberg uncertainty Principle

11.1 Dual behaviour of matter

de Broglie proposed that matter should also exhibit dual behaviour i.e. both particle and wave like properties.

$$\lambda = \frac{h}{mv} = \frac{h}{p} = \frac{h}{\sqrt{2m(KE)}} = \frac{h}{\sqrt{2mqV}}$$

Where p is linear momentum of a particle.

According to de Broglie, every object in motion has a wave character. The wavelengths associated with ordinary objects are so short (because of their large masses) that their wave properties cannot be detected. The wavelengths associated with electrons and other subatomic particles (with very small mass) can however be detected experimentally.

11.2 Heisenberg's Uncertainty Principle

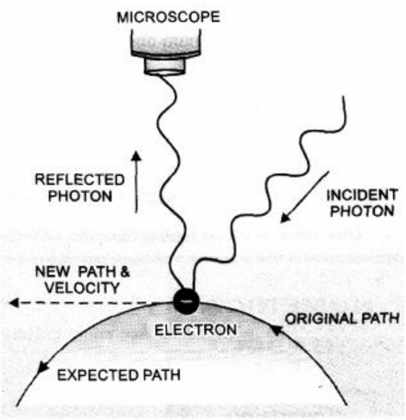
It is impossible to measure simultaneously the position and momentum of a small particle with absolute accuracy. If an attempt is made to measure any of these two quantities with higher accuracy, the other becomes less accurate. The product of the uncertainty in the position (Δx) and the uncertainty in momentum (Δp) is always a constant and is equal to or greater than h/4π.

$(\Delta x).(\Delta p) \geq h/4\pi$

Or $(\Delta x).(m\Delta v) \geq h/4\pi$

Or $(\Delta x).(\Delta x) \geq h/4\pi m$

11.2.1 Explaination



Change of momentum and position of electron on impact with a photon

Suppose we attempt to measure both the position and momentum of an electron. To pin point the position of the electron we have to use light so that the photon of light strikes the electron and the reflected photon is seen in the microscope. As a result of the hitting, the position as well as the velocity of the electron are disturbed.

11.2.2 Significance of Uncertainity Principle:

It rules out the existence of definite paths or trajectories of electrons as stated in Bohr's Model.

Note..

The effect of Heisenberg Uncertainty Principle is significant only for motion of microscopic objects, and is negligible for that of macroscopic objects.

12. QUANTUM MECHANICAL MODEL OF ATOM

Quantum mechanics is a theoretical science that deals with the study of the motion of microscopic objects which have both particle like and wave like properties. The fundamental equation of quantum mechanics was developed by Schrodinger.

This equation describes a function called **electron wave function (ψ)**. This wave function stores all the information about an electron like energy, position, orbital etc. As such it does not have any physical significance. The information stored in ψ about an electron can be extracted in terms of **Quantum Numbers.**

12.1 Probability Density

$|\psi|^2$ is the probability of finding the electron at a point within an atom.

12.2 Concept of Orbital

It is a three dimensional space around the nucleus within which the probability of finding an electron of given energy is maximum (say upto 90%).

12.3 Quantum Numbers

They may be defined as a set of four numbers with the help of which we can get complete information about all the electrons in an atom i.e. location, energy, type of orbital occupied, shape and orientation of that orbital etc.

The three quantum numbers called as Principal, Azimuthal and Magnetic quantum number are derived from Schrodinger wave equation. The fourth quantum number i.e. the Spin quantum number was proposed later on.

1) Principal Quantum Number (n):

It tells about the **shell** to which an electron belongs.

n = 1,2,3,4,5..... and so on.

This number helps to explain the **main lines of the spectrum** on the basis of electronic jumps between these shells.

(a) It gives the **average distance** of the electron from the nucleus. Larger the value of n, larger is the distance from the nucleus.

(b) It completely determines the **energy** in hydrogen atom or hydrogen like species.

The energy of H-atom or H-like species depends only on the value of n.

Order of energy : $1 < 2 < 3 < 4 < 5$....... and so on.

For multi-electron species, energy depends on both principal and azimuthal quantum number.

The maximum number of electrons present in any shell = $\mathbf{2n^2}$

2) Azimuthal Quantum Number (*l*) :

Also known as **Orbital Angular momentum** or **Subsidiary quantum number.** Within the same shell, there are number of sub-shells, so number of electronic jumps increases and this explains the presence of fine lines in the spectrum. This quantum number tells about :

(a) The number **of subshells** present in a shell.

(b) Angular momentum of an electron present in subshell.

(c) **Shapes** of various subshells present within the same shell.

(d) Relative energies of various subshells.

Value of *l* varies from 0 to n – 1

For 1st shell (n = 1): l = 0

For 2nd shell (n = 2): l = 0,1

For 3rd shell (n = 3): l = 0,1,2

For 4th shell (n = 4): l = 0,1,2,3

Value of I	Designation of subsheII
0	s
1	p
2	d
3	f
4	g
5	h

The notations s,p,d,f represent the initial letters of the word sharp, principal, diffused and fundamental. In continuation *l* = 4 is called g subshell and *l* = 5 is called h subshell and so on.

Principal shell	Subshells
1st shell	*l* = 0 (s-subshell)
2nd shell	*l* = 0,1 (s & p subshell)
3rd shell	*l* = 0,1,2 (s,p & d subshell)
4th shell	*l* = 0,1,2,3 (s,p,d & f subshell)

Note..

The number of subshells present in any principal shell is equal to the number of the principal shell.

Energies of various subshell present within the same shell is: s < p < d < f

Angular momentum of an electron in orbital :

$$\frac{h}{2\pi}\sqrt{l(l+1)} = \hbar\sqrt{l(l+1)}$$

(3) Magnetic Quantum Number(m):

This quantum number is required to explain the fact that when the source producing the line spectrum is placed in a magnetic field, each spectral line splits up into a number of line (Zeeman effect).

Under the influence of external magnetic field, electrons of a subshell can orient themselves in a certain preferred regions of space around the nucleus called orbitals.

The magnetic quantum number determines the number of preffered orientations of the electrons present in a subshell. Since each orientation corresponds to an orbital, thus magnetic quantum number determines the **number of orbitals** present in any subshell.

Value of m ranges from – *l* to +*l* including zero.

Sub-shell	Orbitals (m)	Number of orbitals
s-subshell (*l*=0)	m = 0	1
p-subshell (*l*=1)	m = -1, 0, 1	3
d-subshell (*l*=2)	m = –2, –1, 0, 1 ,2	5
f-subshell (*l*=3)	m = –3, –2, –1, 0, 1, 2, 3	7

Orbital	Value of m
P_x	m = 0
P_y	m = + 1
P_z	m = – 1

Orbital	Value of m
d_{z^2}	m = 0
d_{xz}	m = + 1
d_{yz}	m = – 1
$d_{x^2-y^2}$	m = + 2
d_{xy}	m = – 2

These orbitals of the same subshell having equal energy are called **degenerate orbitals.** Eg.

The three p-orbitals of a particular principal shell have the same energy in the absence of magnetic field.

Similarly, all five orbitals of d-subshell of a particular shell have the same energy.

Thus, for H-atom order of energy is:

1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < ....

For multi electron atoms, the energy of the orbitals decreases with increase in effective nuclear charge. Eg

$$E_{2s}(H) > E_{2s}(Li) > E_{2s}(Na) > E_{2s}(K)$$

The total possible values of m in a given subshell = 2*l* + 1

Total no. of orbitals in a given shell = n^2

4) Spin Quantum Number(s):

The electron in an atom not only moves around the nucleus but also spins about its own axis. Since the electron in an orbital can spin either in clockwise or anti-clockwise direction. Thus s can have only two values

$$+\frac{1}{2} \text{ or } -\frac{1}{2}$$

This quantum number helps to explain the magnetic properties of substances.

Note..

An orbital cannot have more than two electrons and these electrons should be of opposite spin.

Thus, maximum number of electrons in s-subshell = 2

Maximum number of electrons in p-subshell = 6

Maximum number of electrons in d-subshell = 10

Maximum number of electrons in f-subshell = 14

12.4 Shapes of atomic orbitals

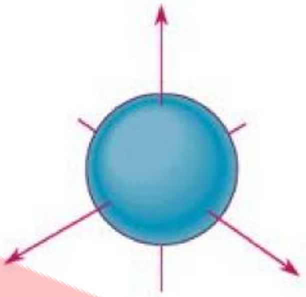
(1) Shape of s-orbitals:

(a) They are non-directional and spherically symmetric i.e. probability of finding the electron at a given distance is equal in all directions.

(b) 1s orbital and 2s orbital have same shape but size of 2s is larger.

(c) There is a spherical shell within 2s orbital where electron density is zero and is called a node.

(d) The value of azimuthal quantum number(l) is zero (l=0) and magnetic quantum number can have only one value i.e. m = 0



(2) Shape of p-orbitals:

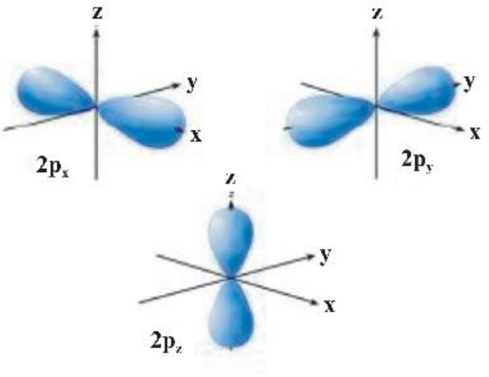
(a) It consists of two lobes present on either side of the plane that passes through the nucleus. The p-orbital is dumb-bell shaped.

(b) There are three possible orientations of electron cloud in p-orbitals. Therefore, the lobes of p-orbital may be considered to be along x,y and z axis. Hence they are designated as p_x, p_y, p_z. The three p-orbitals are oriented at right angles to one another.

(c) First main energy level(Principal quantum number n = 1) does not contain any p-orbital.

(d) The three p-orbitals of a particular energy level have same energy in absence of an external electric and magnetic field and are called degenerate orbitals.

(e) Like s orbitals, p-orbitals increase in size with increase in the energy of main shell of an atom. Thus, value of azimuthal quantum number is one (l=1) and magnetic quantum number has three values (m= –1, 0, +1)



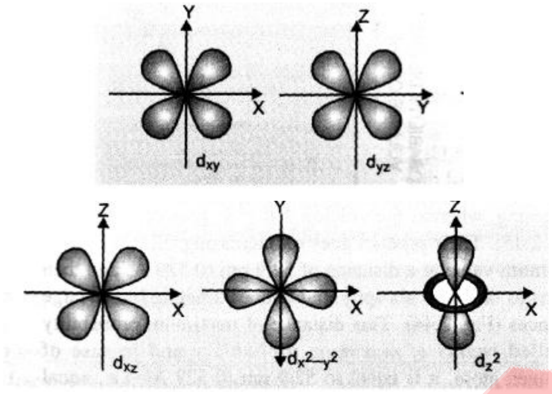
(3) Shapes of d-orbitals:

(a) They are designated as d_{xy}, d_{yz}, d_{zx} and $d_{x^2-y^2}$. They have a shape like a four leaf clover. The fifth d orbital designated as d_{z^2} looks like a doughnut.

(b) All five d orbitals have same energy in the absence of magnetic field.

(c) The d orbitals have azimuthal quantum number $l = 2$ and magnetic quantum number values –2, –1,0,+ 1,+ 2.

(d) For principal shell number 1 and 2, there are no d orbitals.



We have drawn boundary surface diagrams i.e the surface is drawn in space for an orbital on which probability density $(\psi)^2$ is constant. It encloses the region where probability of finding the electron is very high. We do not draw a boundary surface diagram that encloses 100% probability of finding the electron because probability density has some value, howsoever small it may be, at any finite distance from the nucleus. Thus it is not possible to draw a boundary surface diagram of a rigid size in which the probability of finding the electron is 100%.

12.5 Nodes and nodal planes

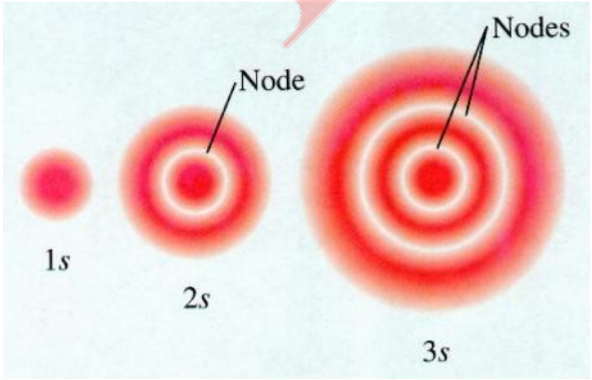
Node:

It is a region of zero probability.

There are two types of nodes:

(1) Radial or Spherical nodes: Three dimensional regions in an orbital where probability of finding the electron becomes zero.

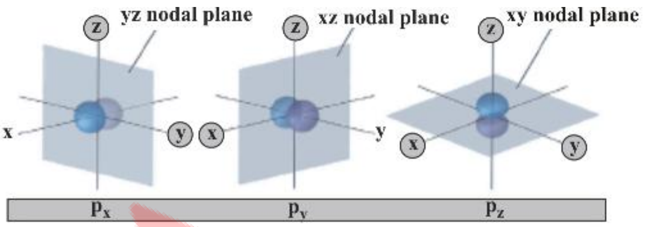
Number of radial/ spherical nodes = n – l – 1



(2) Planar or Angular Nodes: They are the planes cutting through the nucleus on which probability of finding the electron is zero.

Number of Planar/Angular Nodes: l

Total Number of nodes: n - 1



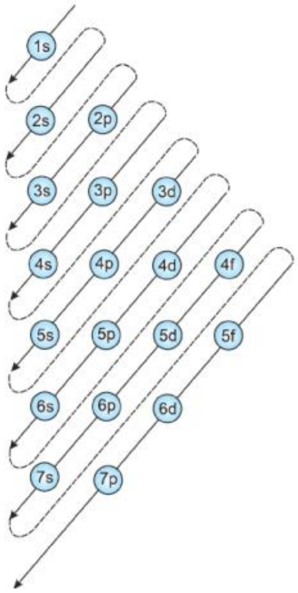
12.6 Filling of orbitals in an atom

(1) Aufbau Principle:

In the ground state of the atoms, the orbitals are filled in order of their increasing energies. In other words, electrons first occupy the lowest energy orbital available to them and enter into higher energy orbitals only when the lower energy orbitals are filled.

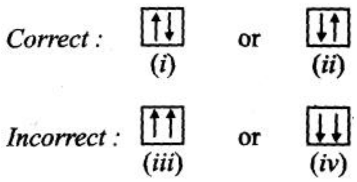
Unlike H-atom where energy of orbitals depend only on n, energy of orbitals of multi-electron orbitals depend on both n and l. Their order of energy can be determined using **(n+l) rule.**

According to this rule, lower the value of (n+l) for an orbital, lower is its energy. If two different types of orbitals have the same value of (n+l), the orbital with lower value of n has lower energy.



$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2$**......**

(2) **Pauli Exclusion Principle:** An orbital can have maximum two electrons and these must have opposite spin.



(3) **Hund's rule of maximum multiplicity:** Electron pairing in p,d and f orbitals cannot occur until each orbital of a given subshell contains one electron each. Also all the singly occupied orbitals will have **parallel spin.**

Electronic configurations of elements in the ground state

Atomic No.	Element	Electronic Config
1	H	$1s^1$
2	He	$1s^2$
3	Li	[He] $2s^1$
4	Be	[He] $2s^2$
5	B	[He] $2s^2\ 2p^1$
6	C	[He] $2s^2\ 2p^2$
7	N	[He] $2s^2\ 2p^3$
8	O	[He] $2s^2\ 2p^4$
9	F	[He] $2s^2\ 2p^5$
10	Ne	[He] $2s^2\ 2p^6$
11	Na	[Ne] $3s^1$
12	Mg	[Ne] $3s^2$
13	Al	[Ne] $3s^2\ 3p^1$
14	Si	[Ne] $3s^2\ 3p^2$
15	P	[Ne] $3s^2\ 3p^3$
16	S	[Ne] $3s^2\ 3p^4$
17	Cl	[Ne] $3s^2\ 3p^5$
18	Ar	[Ne] $3s^2\ 3p^6$
19	K	[Ar] $4s^1$
20	Ca	[Ar] $4s^2$
21	Sc	[Ar] $3d^1\ 4s^2$
22	Ti	[Ar] $3d^2\ 4s^2$
23	V	[Ar] $3d^3\ 4s^2$

24	Cr	[Ar] $3d^5\,4s^1$
25	Mn	[Ar] $3d^5\,4s^2$
26	Fe	[Ar] $3d^6\,4s^2$
27	Co	[Ar] $3d^7\,4s^2$
28	Ni	[Ar] $3d^8\,4s^2$
29	Cu	[Ar] $3d^{10}\,4s^1$
30	Zn	[Ar] $3d^{10}\,4s^2$

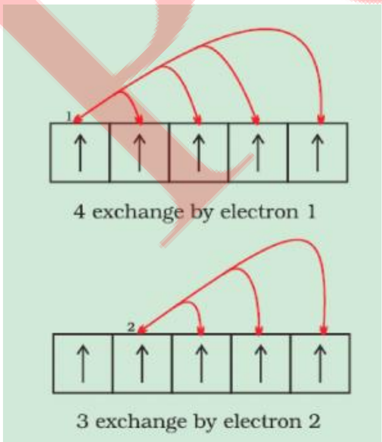
12.7 Exceptional Configuration of Cr & Cu

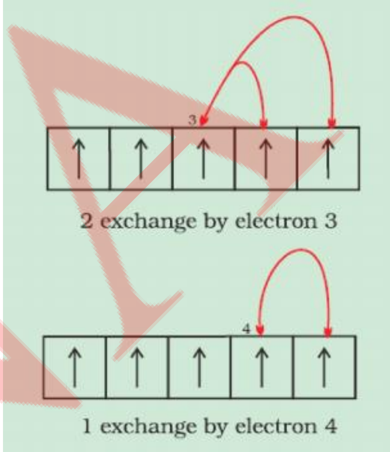
The completely filled and completely half filled sub-shells are stable due to the following reasons:

1. **Symmetrical distribution of electrons*:*** It is well known that symmetry leads to stability. The completely filled or half filled subshells have symmetrical distribution of electrons in them and are therefore more stable. Electrons in the same subshell (here *3d*) have equal energy but different spatial distribution. Consequently, their shielding of one another is relatively small and the electrons are more strongly attracted by the nucleus.

2. **Exchange Energy *:*** The stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a subshell. These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is either half filled or completely filled. As a result the exchange energy is maximum and so is the stability.

eg. for Cr : [Ar] $4s^1\,3d^5$





Thus, total number of exchanges=10

12.8 Electronic Configuration of Ions

12.8.1 Cations:

They are formed when outermost electrons are removed from an atom. While removing the electrons, we must remove the electrons from the highest principal quantum number.

12.8.2 Anions:

They are formed when electrons are added to the innermost empty shell.

12.8.3 Magnetic moment :

$$\sqrt{n(n+2)}\ \text{B.M.}$$

B.M. → Bohr Magneton

Where n is number of unpaired electrons.

Species with unpaired electrons are called **paramagnetic** and the species with no unpaired electrons are called **diamagnetic**

13. IMPORTANT RELATIONS

Rydberg equation : $\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$(R_H = 109678\ \text{cm}^{-1} \text{ and } n_2 > n_1)$

$c = \lambda \times \upsilon \text{ and } \bar{v} = \frac{1}{\lambda}$

$E = h\nu \text{ or } = \frac{hc}{\lambda}$

Bohr's Model

$$E_n = \frac{-1312Z^2}{n^2}\text{kJ mol}^{-1}$$

$$= \frac{-2.178 \times 10^{-18} Z^2}{n^2}\text{J / atom} = \frac{-13.6Z^2}{n^2}\text{eV / atom}$$

Velocity of electron, $\upsilon_n = \frac{2.165 \times 10^6 Z}{n}\text{ m / s}$

Radius of orbit $= \frac{0.529\ n^2}{Z}$ Å

Photoelectric effect = $h\nu = h\nu_0 + \frac{1}{2}mv^2$

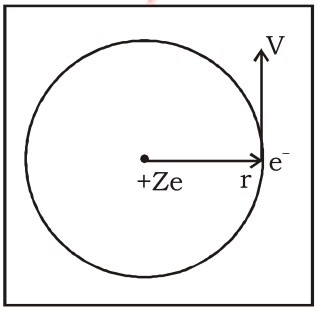
$(\nu_0 = \text{Threshold frequency})$

de-Broglie equation : $\lambda = \frac{h}{m\nu}$

Heisenberg's uncetainity principle : $\Delta x \times \Delta p \geq \frac{h}{4\pi}$

14. MATHEMATICAL MODELLING OF BOHR's POSTULATES

Consider an ion of atomic number (Z) containing single electron revolving its nucleus at a distance of 'r' as shown in the figure.



Note..

Atomic number = Number of protons on the nucleus = Z

⇒ Charge on the nucleus = + Ze

Electrostatic force of attraction (F) between the nucleus of charge + Ze and electron (–e) is given by :

$F = \frac{K|q_1||q_2|}{r^2}$ where $K = \frac{1}{4\pi\varepsilon_0}$

$= 9 \times 10^9\ \text{Nm}^2\text{C}^{-2}$

$F = \frac{K|Ze||-e|}{r^2} = \frac{KZe^2}{r^2}$ ....(i)

The centrifugal forces acting on the electron is $\frac{mv^2}{r}$ ....(ii)

This centrifugal force must be provided by the electrostatic force of attraction (F).

⇒ From (i) and (ii), we have :

$\frac{KZe^2}{r^2} = \frac{mV^2}{r}$ ....(iii)

Angular momentum of electron about the nucleus = $mVr = \frac{nh}{2\pi}$ .... (iv)

where 'n' is a positive integer

$(n = 1, 2, 3, \ldots\ldots\ldots \infty)$

Solve (iii) and (iv) to get :

$V = \frac{2\pi KZe^2}{nh}$ and $r = \frac{n^2h^2}{4\pi^2\ Kme^2Z}$

put $K = 9 \times 10^9\ \text{Nm}^2\text{C}^{-2}$, $e = 1.6 \times 10^{-19}$C and $h = 6.63 \times 10^{-34}$ Js in the above expressions to get :

Velocity of an electron in nth Bohr orbit ø

$$\mathbf{V_n = 2.165 \times 10^6 \frac{Z}{n}\ ms^{-1}}$$

and Radius of the nth Bohr orbit ø $\mathbf{r_n = 0.53 \frac{n^2}{Z}}$ **Å**

Now, the Total Energy of the electron moving in nth orbit ≡ K.E.$_n$ + E.P.E.$_n$

$$\text{T.E.}_n = \frac{1}{2}mV_n^2 + \frac{K(Ze)(-e)}{r} \quad \left[\because \text{E.P.E.} = \frac{K\,q_1\,q_2}{r}\right]$$

$$\Rightarrow \quad T.E_n = \frac{1}{2}\left(\frac{K\,Ze^2}{r_n}\right) + \frac{K(Ze)(-e)}{r_n} \qquad [\text{Using (iii)}]$$

$$\Rightarrow \quad \mathbf{E_n \equiv T.\,E_n = \frac{-KZe^2}{2r_n}}$$

It can be shown from the above expressions that :

$$K.E._n = \frac{1}{2}\frac{K\,Ze^2}{r_n},\ P.E._n = \frac{-K\,Ze^2}{r_n} \text{ and } E_n = \frac{-K\,Ze^2}{2r_n}$$

or $K.E._n = -E_n$ and $E.P.E._n = 2E_n$

Using the value of r_n in the expression of $E_{n,}$ we get :

$$E_n = \frac{-2\pi^2\,K^2me^4Z^2}{n^2h^2}$$

$$\mathbf{E_n \equiv -2.178\times10^{-18}\frac{Z^2}{n^2}\,\text{J/atom}}$$

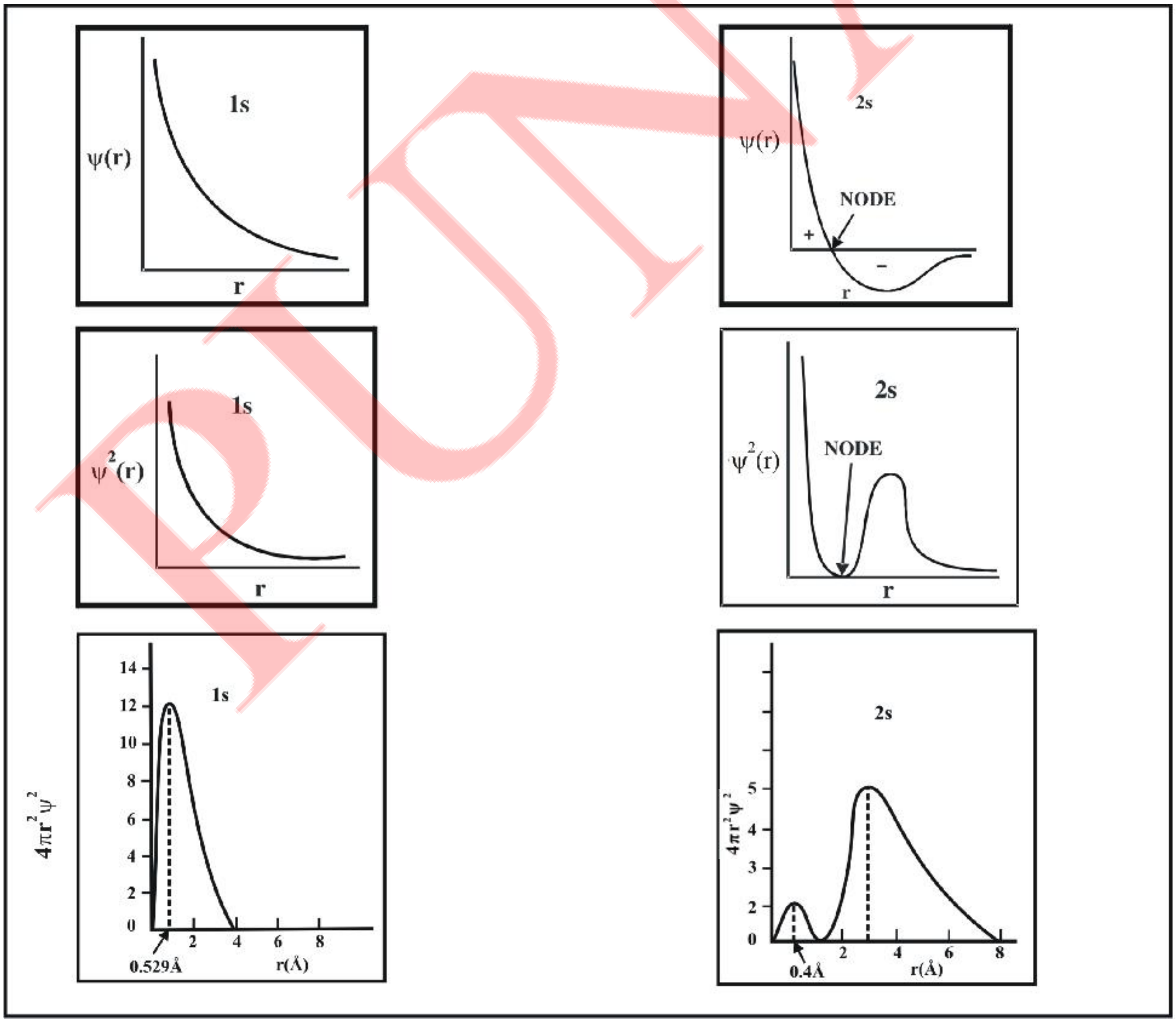
$$\text{or }\ \mathbf{E_n \equiv -13.6\frac{Z^2}{n^2}\,\text{eV/atom}}$$

$$\left[\because 1\text{eV} = 1.6\times10^{-19}\,\text{J}\right]$$

$$\equiv -2.178\times10^{-18}\,\frac{Z^2}{n^2}\times 6.02\times10^{23}\ \text{J/mole}$$

$$\mathbf{ø\; -\; 1312\;\frac{Z^2}{n^2}\;\text{kJ/mole}}$$

15. PROBABILITY DISTRIBUTION DIAGRAMS FOR 1s AND 2s



PERIODIC CLASSIFICATION

1. INTRODUCTION

Periodic table may be defined as the table which classifies 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.

2. HISTORICAL DEVELOPMENT OF THE PERIODIC TABLE

All earlier attempts of the classification of the elements were based upon their atomic weights.

2.1 Dobereiner's Triads

In 1829, Dobereiner classified certain elements in the groups of three called **triads**. The three elements in a triad had similar chemical properties. When the elements in a triad were arranged in the order of increasing atomic weights, the atomic weight of the middle element was found to be approximately equal to the arithmetic mean of the other two elements.

1. Triad	**Iron**	**Cobalt**	**Nickel**	**Mean of 1st and 3rd**
At. wt.	55.85	58.93	58.71	Atomic weights are nearly the same
2. Triad	**Lithium**	**Sodium**	**Potassium**	$\frac{7+39}{2}=23$
At. wt.	7	23	39	
3. Triad	**Chlorine**	**Bromine**	**Iodine**	$\frac{35.5+127}{2}=81.25$
At. wt.	35.5	80	127	
4. Triad	**Calcium**	**Strontium**	**Barium**	$\frac{40+177}{2}=88.5$
At. wt.	40	87.5	137	

2.2 Newland's Law of Octaves

In 1865, an English chemist, *John Alexander Newlands* observed that

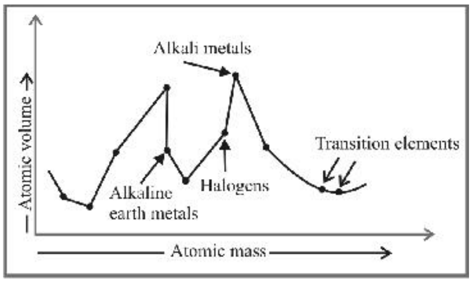
When the lighter elements were arranged in order of their increasing atomic weights, the properties of every eighth element were similar to those of the first one like the eighth note of a musical scale. This generalization was named as ***Newlands's law of octaves.***

Element	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**
At. wt.	7	9	11	12	14	16	19
Element	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
At. wt.	23	24	27	29	31	32	35.5
Element	**K**	**Ca**					
At. wt.	39	40					

2.3 Lothar Meyer's Curve

"Physical properties of elements are periodic functions of their atomic masses."

According to Lothar Meyer, elements having similar properties occupy the similar positions in atomic volume viz atomic mass curve



2.4 Mendeleev's Periodic Law

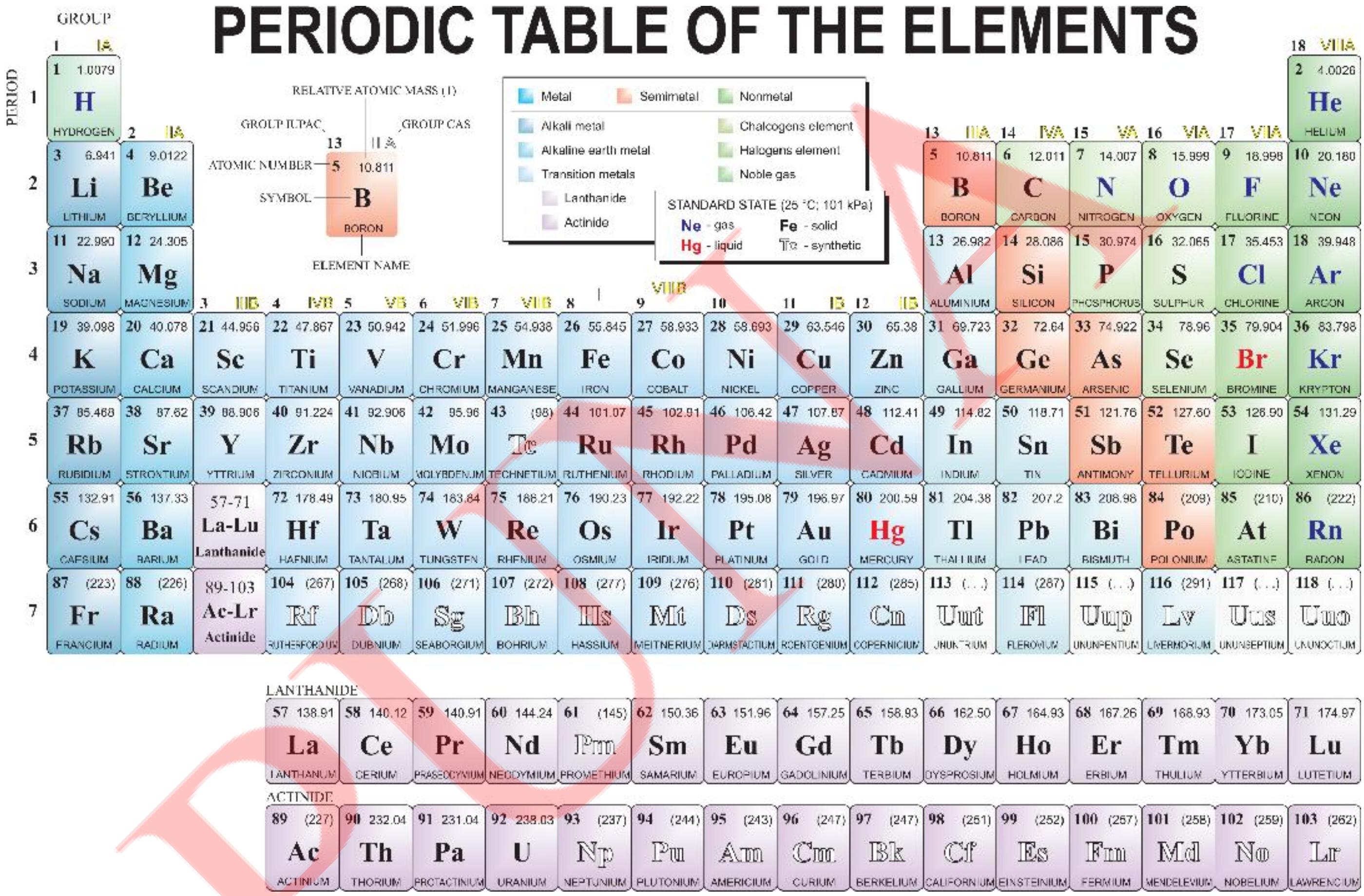
Mendeleev arranged elements in horizontal rows and vertical columns of a table in order of their increasing atomic weights in such a way that the elements with similar properties occupied the same vertical column or group.

2.5 Modern Periodic Law

In 1913, the English physicist, Henry Moseley observed regularities in the characteristic X-ray spectra of the elements. A plot of $\sqrt{v}$ (where v is frequency of X-rays emitted) against **atomic number** (Z) gave a straight line and not the plot of $\sqrt{v}$ vs atomic mass.

Mendeleev's Periodic Law was, therefore, accordingly modified. This is known as the **Modern Periodic Law** and can be stated as :

The physical and chemical properties of the elements are periodic functions of their atomic numbers.



PERIODIC TABLE OF THE ELEMENTS

PERIOD	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 H HYDROGEN																	2 4.0026 He HELIUM
2	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM											5 10.811 B BORON	6 12.011 C CARBON	7 14.007 N NITROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICON	15 30.974 P PHOSPHORUS	16 32.065 S SULPHUR	17 35.453 Cl CHLORINE	18 39.948 Ar ARGON
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.38 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.798 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.96 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (267) Rf RUTHERFORDIUM	105 (268) Db DUBNIUM	106 (271) Sg SEABORGIUM	107 (272) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (276) Mt MEITNERIUM	110 (281) Ds DARMSTADTIUM	111 (280) Rg ROENTGENIUM	112 (285) Cn COPERNICIUM	113 (...) Uut UNUNTRIUM	114 (287) Fl FLEROVIUM	115 (...) Uup UNUNPENTIUM	116 (291) Lv LIVERMORIUM	117 (...) Uus UNUNSEPTIUM	118 (...) Uuo UNUNOCTIUM

LANTHANIDE

57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.05 Yb YTTERBIUM	71 174.97 Lu LUTETIUM

ACTINIDE

89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM

Classification of Modern Periodic Table

s-block
Left
IA, IIA
IA → alkali (ns^1)
IIA → alkaline earth metal (ns^2)
ns^{1-2}

p-block
Right
IIIA-VIIA, VIII
13-18
VIA/16 → chalcogens
VIIA/17 → Halogens
0/18 → Inert gases
ns^2np^{1-6}

d-block
middle
3 → 1 &
IIIB → VIIB
VIII, IB, IIB
transition element
$(n-1)d^{1-10}\ ns^{0-2}$

f-block
Bottom
Inner transition element
$(n-2)f^{1-14}\ (n-1)d^{0-2}\ ns^2$

Nomenclature of elements with Atomic Numbers > 100

The naming of the new elements had been traditionally the privilege of the discoverer and the suggested name was ratified by the IUPAC.

Table : Notation for IUPAC Nomenclature of Elements

Digit	Name	Abbreviation
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

Table : Nomenclature of Elements with Atomic Number Above 100

Atomic Number	Name	Symbol
101	Unnilunium	Unu
102	Unnibium	Unb
103	Unniltrium	Unt
104	Unnilquadium	Unq
105	Unilpentium	Unp
106	Unnilhexium	Unh
107	Unnilseptium	Uns
108	Unniloctium	Uno
109	Unnilennium	Une
110	Ununnillium	Uun

3. PREDICTION OF BLOCK, PERIOD & GROUP

1. What electronic configuration
2. Block - last e^- enters into which orbital
3. Period - Max value of principal quantum number

Group - s block - no. of valence electron

p block - 10 + no. of valence electron

d block – ns + no. of (n – 1) d e^-

f block – III B

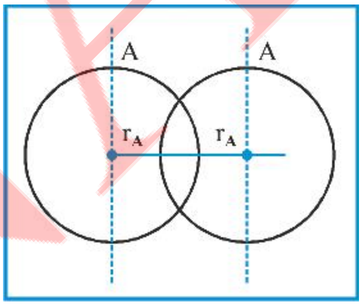
4. PROPERTIES OF AN ELEMENT

4.1 Atomic Radius

We cannot measure the exact size of an isolated atom because its outermost electron have a remote chance of being found quite far from the nucleus. So different types of atomic radius can be used based on the environment of atoms i.e; **covalent** radius, **van der Waals'** radius, **metallic** radius.

4.1.1 Covalent Radius

The half of the distance between the nuclei of two identical atoms joined by single covalent bond in a molecule is known as **covalent radius.**



So covalent radius for A-A

$$\boxed{r_A = \frac{d_{A-A}}{2}}$$

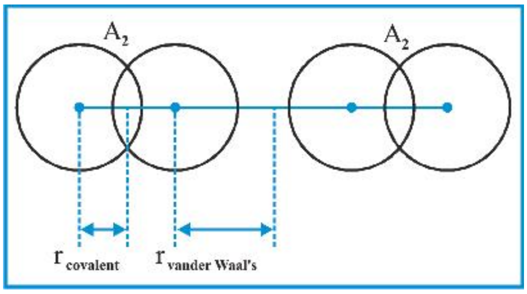
If covalent bond is formed between two different elements then

$$\boxed{d_{A-B} = r_A + r_B - 0.09\,(\chi_A - \chi_B)}$$

where χ_A and χ_B are electronegative of A and B

4.1.2 Vander Waal's Radius

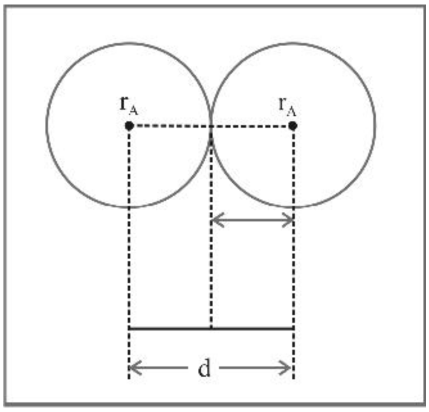
It is half of the internuclear distance between adjacent atoms of the two neighbouring molecules in the solid state.



$$r_{vander\ waal} = \frac{d_{A-A}}{2}$$

4.1.3 Metallic Radius (Crystal radius)

It is one-half of the distance between the nuclei of two adjacent metal atoms in the metallic crystal lattice.



So metallic radius for A-A

$d = r_A + r_A$

$$\boxed{r_A = \frac{d}{2}}$$

$$\boxed{{}^{*}\ \mathbf{r_{covalent} < r_{metallic} < r_{vander\ waals}}}$$

4.2 Variation of Atomic Radii in the Periodic Table

(a) Variation along a period

In general, the covalent and van der Waals radii decrease with increase in atomic number as we move from left to right in a period.

4.3 Atomic Radii

(a) Variation along a period

It is because with in the period the outer electrons are in the same valence shell & the **effective nuclear charge** increases as the atomic number increases resulting in the increased attraction of electrons to the nucleus.

(b) Variation along a group

Atomic radius in a group increase as the atomic number increases. It is because with in the group, the principal quantum number (n) increases and the valence electrons are farther from the nucleus.

(c) Ionic Radius

The removal of an electron from an atom results in the formation of a **cation**, whereas gain of an electron leads to an **anion**.

In general, the ionic radii of elements exhibit the same trend as the atomic radii. A cation is **smaller** than its parent atom because it has fewer electrons while its nuclear charge remains the same. The size of an anion will be **larger** than that of the parent atom because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge. For example, the ionic radius of fluoride ion (F^-) is 136 pm whereas the atomic radius of fluorine is only 64 pm. On the other hand ,the atomic radius of sodium is 186 pm compared to the ionic radius of 95 pm for Na^+.

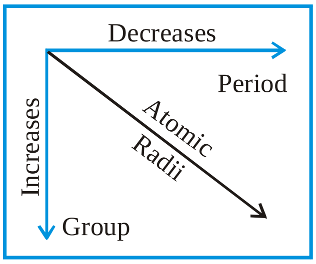
(d) Isoelectronic Species

Isoelectronic species are those which have same number of electrons. For example, O^{2-}, F^-, Na^+ and Mg^{2+} have the same number of electrons (10). Their radii would be different because of their different nuclear charges. The cation with the greater positive charge will have a smaller radius because of the greater attraction of the electrons to the nucleus. Anion with the greater negative charge will have the larger radius. In this case, the net repulsion of the electrons will outweigh the nuclear charge and the ion will expand in size.

Order of atomic radii is

$$\boxed{\mathbf{Mg^{2+} < Na^+ < F^- < O^{2-}}}$$

General Trend :



4.4 Ionization Energy

The minimum amount of energy required to remove the electron from the outermost orbit of an isolated atom in the gaseous state is known as ionization energy.

$$M \xrightarrow[-e^-]{IE_1\ \text{(First Ionization Energy}} M^+ \xrightarrow[-e^-]{IE_2} M^{2+} \xrightarrow[-e^-]{IE_3}$$

$$M^{3+} \xrightarrow[-e^-]{IE_4} M^{4+}$$

IE_1, IE_2, IE_3 and IE_4 are successive ionization energies.

$$\boxed{\begin{array}{l} \quad IE_4 > IE_3 > IE_2 > IE_1 \\ \text{or} \quad \Delta_i H_4 > \Delta_i H_3 > \Delta_i H_2 > \Delta_i H_1 \end{array}}$$

Variation of Ionisation Energy in Periodic Table

(a) Variation along a period

In a period, the value of ionisation enthalpy increases from left to right with breaks where the atoms have somewhat stable configurations. The observed trends can be easily explained on the basis of increased nuclear charge and decrease in atomic radii. Both the factors increase the force of attraction towards nucleus and consequently, more and more energy is required to remove the electrons and hence, ionisation enthalpies increase.

(b) Variation along a group

On moving the group, the atomic size increases gradually due to an addition of one new principal energy shell at each succeeding element. On account of this, the force of attraction towards the valence electrons decreases and hence the ionisation enthalpy value decreases.

4.5 Units of I.E./I.P.

It is measured in units of electron volts (eV) per atom or kilo calories per mole (kcal mol^{-1}) or kilo Joules per mole (kJ mol^{-1}). One electron volt is the energy acquired by an electron while moving under a potential difference of one volt.

1 electron volt (eV) per atom

$= 3.83 \times 10^{-20}$ cal per atom

$= 1.602 \times 10^{-19}$ J per atom (1 cal = 4.184 J)

$= 3.83 \times 10^{-20} \times 6.023 \times 10^{23}$ cal mol^{-1}

$= 23.06$ kcal mol^{-1}

$= 1.602 \times 10^{-19} \times 6.023 \times 10^{23}$ J mol^{-1}

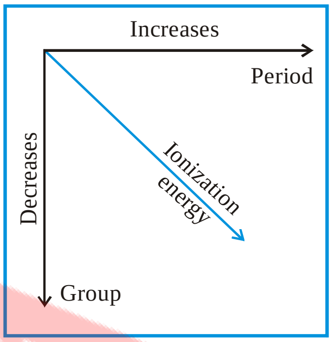
$= 96.49$ kJ mol^{-1}

$\therefore$ 1 electron volt (eV) per atom

$= 23.06$ kcal mol^{-1} $= 96.49$ kJ mol^{-1}

Important Points

- * Ionization energy increases with decreasing the size of an atom or an ion
- * Ionization energy increases with decreasing screening effect.
- * Ionization energy increases with increasing nuclear charge
- * Ionization energy increases if atom having half filled and fully filled orbitals
- * The penetrating power of orbitals is in the order s > p > d > f



Electron Gain Enthalpy

When an electron is added to a neutral gaseous atom (X) to convert it into a negative ion, the enthalpy change accompanying the process is defined as the **Electron Gain Enthalpy (a$_{eg}$H)**. Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion as represented by

X(g) + e$^-$ ì X$^-$(g)

Depending on the element, the process of adding an electron to the atom can be either **endothermic** or **exothermic**. For many elements energy is released when an electron is added to the atom and the electron gain enthalpy is negative. For example, group 17 elements (the **halogens**) have very **high negative electron gain enthalpies** because they can attain stable noble gas electronic configurations by picking up an electron. On the other hand, **noble gases** have large **positive** electron gain enthalpies because the electron has to enter the next higher principal quantum level leading to a very unstable electronic configuration.

Variation of Electron Gain Enthalpy

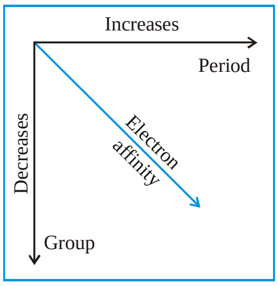
(a) Variation along a period

Electron gain enthalpy becomes more and more negative from left to right in a period. This is due to decrease in size and increase in nuclear charge as the atomic number increases in a period. Both these factors favour the addition of an extra electron due to higher force of attraction by the nucleus for the incoming electron.

(b) Variation along a group

The electron gain enthalpies, in general, become less negative in going down from top to bottom in a group. This is due to increase in size on moving down a group.

This factor is predominant in comparison to other factor, i.e., increase in nuclear charge.



4.6 Electronegativity

The tendency of an atom to attract the shared pair of electrons towards itself is known as its **electronegativity**.

According to **Pauling**, the electronegativity of F is 4.0 and electronegativity of other elements can be calculated as

$(\chi_A - \chi_B) = 0.208\,[E_{A-B} - (E_{A-A} \times E_{B-B})^{1/2}]^{1/2}$

According to **Mulliken**

$$\boxed{\text{Electronegativity} = \frac{IP + EA}{2}}$$

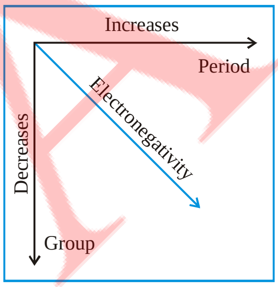
(where IP = Ionization potential, EA = Electron affinity)

If IP and EA are taken in electron volt

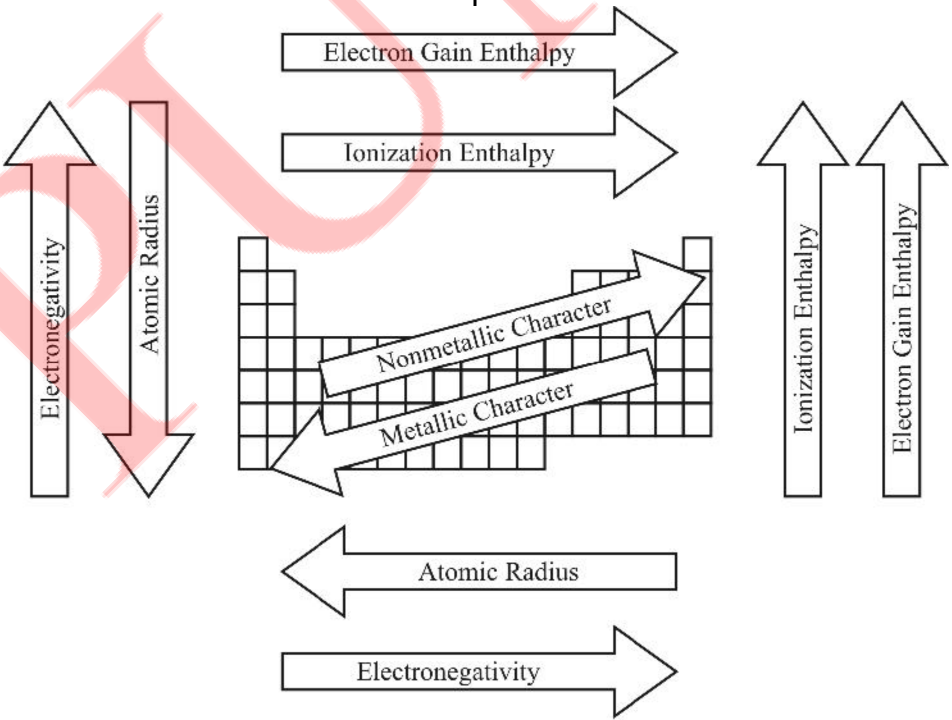
* Percentage ionic character $= 16\,(\chi_A - \chi_B) + 3.5\,(\chi_A - \chi_B)^2$ where χ_A and χ_B are electronegativities of A and B.

* If the difference in the electronegatives of combining atoms is 1.7, the bond is 50% covalent and 50% ionic.

* If the difference in electronegativities of oxygen and element is very high the oxide shows a basic character.



The periodic trends of elements in the periodic table



4.7 Periodic Trends in Chemical Properties

4.7.1 Periodicity of Valence or Oxidation States

The electrons present in the outermost shell of an atom are called ***valence electrons*** *and the number of these electrons determine the* ***valence*** *or the* ***valency*** *of the atom. It is because of this reason that the outermost shell is also called the* ***valence shell*** *of the atom and the orbitals present in the valence shell are called* ***valence orbitals****.*

In case of representative elements, the valence of an atom is generally *equal to either the number of valence electrons* (s- and p-block elements) or equal to eight minus the number of valence electrons.

Group	1	2	13	14	15	16	17	18
Number of valence electrons	1	2	3	4	5	6	7	8
Valence	1	2	3	4	3, 5	2, 6	1, 7	0, 8

In contrast, transition and inner transition elements, exhibit variable valence due to involvement of not only the valence electrons but d- or f-electrons as well. However, their most common valence are 2 and 3.

Let us now discuss periodicity of valence along a period and within a group.

(a) Variation along a period

As we move across a period from left to right, the number of valence electrons increases from 1 to 8. But the valence of elements, w.r.t. H or O first increases from 1 to 4 and then decreases to zero.

In the formation of Na_2O molecule, oxygen being more electronegative accepts two electrons, one from each of the two sodium atoms and thus shows an oxidation state of –2. On the other hand, sodium with valence shell electronic configuration as $3s^1$ loses one electron to oxygen and is given an oxidation state of +1. Thus, the *oxidation state of an element in a given compound may be defined as the charge acquired by its atom on the basis of electronegativity of the other atoms in the molecule.*

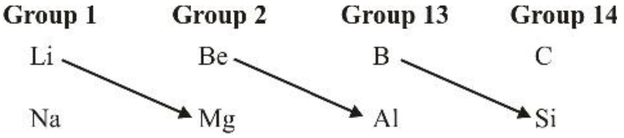
(b) Variation within a group

When we move down the gorup, the number of valence electrons remains the same, therefore, all the elements in a group exhibit the same valence. For example, all the elements of group 1 (alkali metals) have valence one while all the elements of group 2 (alkaline earth metals) exhibit a valence of two.

Noble gases present in group 18 are zerovalent, i.e., their valence is zero since these elements are **chemically inert.**

4.7.2 Anomalous Properties of Second Period Elements

It has been observed that *some elements of the second period show similarities with the elements of the third period placed diagonally to each other, though belonging to different groups*. For example, lithium (of group 1) resembles magnesium (of group 2) and beryllium (of group 2) resembles aluminium (of group 13) and so as. *This similarity in properties of elements placed diagonally to each other is called* **diagonal relationship.**



The anomalous behaviour is due to their small size, large charge/radius ratio and high electronegativity of the elements. In addition, the first member of group has only four valence orbitals (2s and 2p) available for bonding, whereas the second member of the groups have nine valence orbitals (3s, 3p, 3d). As a consequence of this, the maximum covalency of the first member of each group is 4 (e.g., boron can only form $[BF_4])^-$, whereas the other members of the groups can expand their valence shell to accommodate more than four pairs of electrons e.g., aluminium forms $[AlF_6]^{3-}$. Furthermore, the first member of p-block elements displays greater ability to form pπ-pπ multiple bonds to itself (e.g., C=C, C≡C, N=N, N≡N) and to other second period elements (e.g., C=O, C=N, C≡N, N=O) compared to subsequent members of the same groups.

4.7.3 Periodic Trends and Chemical Reactivity

Reactivity of Metals

The reactivity of metals is measured in terms of their tendency to lose electrons from their outermost shell.

In a period

The tendency of an element to lose electrons decreases in going from left to right in a period. So, the reactivity of metals decreases in a period from left to right. For example, the reactivity of third period elements follows the order.

$$\underset{\textbf{more reactive}}{\text{Na}} > \text{Mg} > \underset{\textbf{reactive}}{\text{Al}}$$

In a group

The tendency to lose electrons increases as we go down a group. So, the reactivity of metals increases down the group. Thus, in group 1, the reactivity follows the order.

$$\underset{\textbf{Least reactive}}{\text{Li}} < \text{Na} < \text{K} < \text{Rb} < \underset{\textbf{Most reactive}}{\text{Cs}}$$

—— Reactivity increases ⟶

Reactivity of Non-Metals

The reactivity of a non-metal is measured in terms of its tendency to gain electrons to form an anion.

In a period

The reactivity of non-metals increases from left to right in a period. During reaction, non-metals tend to form anions. For example, in the second period, the reactivity of non-metals increases in the order.

$$\underset{\textbf{Less reactive}}{C} < N < O < \underset{\textbf{More reactive}}{F}$$

$$\xrightarrow{\text{Reactivity increases}}$$

In a group

The reactivity of non-metals in a group decreases as we go down the group. This is because the tendency to accept electrons decreases down the group. The reactivity of halogens follows the order

$$\underset{\textbf{Most reactive}}{F} > Cl > Br > \underset{\textbf{Least reactive}}{I}$$

$$\xrightarrow{\text{Reactivity decreases}}$$

The normal oxide formed by the element on extreme left is the **most basic** (e.g., Na_2O) whereas that formed by the element on extreme right is the **most acidic** (e.g., Cl_2O_7). Oxides of elements in the centre are **amphoteric** (e.g., Al_2O_3, As_2O_3) or **neutral** (e.g., CO, NO, N_2O). Amphoteric oxides behave as acidic with bases and as basic with acids, whereas neutral oxides have no acidic or basic properties.

4.7.4 Inert Pair Effect

In groups 13-16, as we move down the group, the tendency of s-electrons of the valence shell to participate in bond formation decreases. This means that lower oxidation state becomes more stable.

Reason: As we go down these groups, the increased nuclear charge outweighs the effect of the corresponding increase in atomic size. The s-electrons thus become more tightly held (more penetrating) and hence more reluctant to participate in bond formation. Hence, the lower oxidation state becomes more stable.

5. SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Mendeleev's periodic table was based on atomic masses of the elements. When Mendeleev presented the periodic table, only 63 elements were known. He left 29 places in the table for unknown elements.

2. Modern Mendeleev periodic table is based on atomic numbers of the elements. The modern periodic law is : **"The physical and chemical properties of the elements are periodic function of their atomic numbers".**

   The horizontal row in the periodic table is called a **period** and vertical column is called **group**. There are seven periods and nine groups in the modern Mendeleev periodic table.

3. The long or extended form of periodic table consists of seven periods and eighteen vertical columns (groups or families). The elements in a period have same number of energy shells, i.e., principal quantum number (n). These are numbered 1 to 7.

1st period	1s	2 elements
2nd period	2s 2p	8 elements
3rd period	3s 3p	8 elements
4th period	4s 3d 4p	18 elements
5th period	5s 4d 5p	18 elements
6th period	6s 4f 5d 6p	32 elements
7th period	7s 7f 6d 7p	32 elements
	Total	*118 elements

   At present 114 elements are known.

   In a vertical column (group), the elements have similar valence shell electronic configuration and therefore exhibit similar chemical properties.

4. There are four blocks of elements: s-, p-, d- and f-block depending on the orbital which gets the last electron. The general electronic configuration of these blocks are :

   s-block : [Noble gas] $ns^{1 \text{ or } 2}$. However, hydrogen has 1s1 configuration.

   p-block : [Noble gas] ns^2np^{1-6}

   d-block : [Noble gas] $(n-1)d^{1-10}ns^{1 \text{ or } 2}$

   f-block : [Noble gas] $(n-2)f^{1-14}(n-1)d^{0 \text{ or } 1}ns^2$

   s-block elements occupy IA(1) and IIA(2) groups, i.e., extreme left portion of the periodic table.

   p-block elements occupy IIIA(13), IVA(14), VA(15), VIA(16), VIIA(17) and VIIIA(18) groups, i.e., right portion of the periodic table.

   d-block elements occupy IIIB(3), IVB(4), VB(5), VIB(6), VIIB(7), VIIB(8, 9 and 10), IB(11) and IIB(12) groups, i.e., central portion of the periodic table. There are four d-block series, i.e., 3d series, 4d series, 5d series and 6d series, each consisting of ten elements, i.e., in all forty d-block elements are present in periodic table.

   f-block elements are accommodated in two horizontal rows below the main periodic table, each row consists of 14 elements, i.e., 28 f-block elements are present in periodic table. The elements in first row are termed 4f-elements or rare earth or lanthanides while the elements of second row are termed 5f-elements or actinides.

5. The elements are broadly divided into three types :

(i) **Metals** comprise more than 78% of the known elements. s-block, d-block and f-block elements are metals. The higher members of p-block are also metals.

(ii) **Non-metals** are less than twenty. (C, N, P, O, S, Se, H, F, Cl, Br, I, He, Ne, Ar, Kr, Xe and Rn are non-metals).

(iii) Elements which lie in the border line between metals and non-metals are called **semimetals** or **metalloids**. B, Si, Ge, As, Sb, Te, Po and At are regarded metalloids.

6. IUPAC given a new scheme for assigning a temporary name to the newly discovered elements. The name is derived directly from the atomic number of the elements. However, IUPAC has accepted the following names of the elements from atomci numbers 104 to 110.

Rutherfordium (Rf),	Dubnium (Db),	Seaborgium (Sg)
104	105	106
Bohrium (Bh),	Hassium (Hs),	Meitnerium (Mt),
107	108	109
Darmstadtium (Ds)		
110		

   The temporary names of the elements discovered recently are :

Unununium (Uuu),	Ununbium (Uub)	
111	112	
Ununquadium (Uuq)	and	Ununhexium (Uuh)
114		116

7. The recurrence of similar properties of the elements after certain definite intervals when the elements are arranged in order of increasing atomic numbers in the periodic table is termed **periodicity**. The cause of periodicity is the repetition of similar electronic configuration of the atom in the valence shell after certain definite intervals. These definite intervals are 2, 8, 8, 18, 18 and 32. These are known as magic number.

   Periodicity is observed in a number of properties which are directly or indirectly linked with electronic configuration.

(i) Effective nuclear charge increases across each period.

(ii) Atomic radii generally decrease across the periods.

(iii) Atomic radii generally increase on moving from top to bottom in the groups.

(iv) Atomic radius is of three types :

(a) **Covalent radius :** It is half of the distance between the centres of the nuclei of two similar atoms joined by a single covalent bond. This is generally used for non-metals.

(b) **Crystal or metallic radius :** It is half of the internuclear distance between two nearest atoms in the metallic lattice. It is generally used for metals.

(c) **van der Waals' radius :** It is half of the internuclear distance between the nearest atoms belonging to two adjacent molecules in solid state.

van der Waals' radius > Metallic radius > Covalent radius (for an atom)

(v) Cations are generally smaller than anions.

(vi) Cations are smaller and anions are larger than neutral atoms of the elements.

Cation size < Neutral atom size < Anion size

(vii) Elements of 2nd and 3rd transition series belonging to same vertical columns are similar in size and properties due to **lanthanide contraction**.

(viii) The first element is each group of the representative elements shows abnormal properties, i.e., differs from other elements of the group because of much smaller size of the atom.

(ix) The ions having same number of electrons but different nuclear charge are called **isoelectronic ions**.

Examples,

(a) N^{3-}, O^{2-}, F^{-}, Na^{+}, Mg^{2+}, Al^{3+}

(b) P^{3-}, S^{2-}, Cl^{-}, K^{+}, Ca^{2+}, Sc^{3+}

In isoelectronic ions, the size decreases if Z/e increases i.e., greater the nuclear charge, smaller is the size of the ion.

(x) The energy required to remove the most loosely held electron from the gaseous isolated atom is termed ionisation enthalpy.

(xi) Ionisation enthalpy values generally increase across the periods.

(xii) Ionisation enthalpy values generally decrease down the group.

(xiii) Removal of electron from filled and half filled shells requires of higher energy. For example, the ionisation enthalpy of nitrogen is higher than oxygen. Be, Mg and noble gases have high values.

(xiv) Metals have low ionisation enthalpy values while non-metals have high ionisation enthalpy values.

(xv) Successive ionisation enthalpies of an atom have higher values.

$IE_{I} < IE_{II} < IE_{III} \ldots$

(xvi) The enthalpy change taking place when an electron is added to an isolated gaseous atom of the element is called electron gain enthalpy. The first electron gain enthalpy of most of the elements is negative as energy is released in the process but the values are positive or near zero in case of the atoms having stable configuration such as Be, Mg, N, noble gases, etc.

(xvii) Electron gain enthalpy becomes more negative from left to right in a period and less negative from top to bottom in a group.

(xviii) Successive electron gain enthalpies are always positive.

(xix) The elements with higher ionisation enthalpy have higher negative electron gain enthalpy.

(xx) Electronegativity is the tendency of an atom to attract the shared pair of electrons towards itself in a bond.

(xxi) Electronegativity increases across the periods and decreases down the groups.

(xxii) Metals have low electronegativities and non-metals have high electronegativities.

(xxiii) Metallic character decreases across the periods and increases down the group.

(xxiv) Valence of an element belonging to s- and p- block (except noble gases) is either equal to the number of valence electrons or eight minus number of valence electrons.

(xxv) The **reducing nature** of the elements decreases across the period while **oxidising nature** increases.

(xxvi) The **basic character** of the oxides decreases while the **acidic character** increases in moving from left to right in a period.

6. SOME IMPORTANT FACTS ABOUT ELEMENTS

(i) Bromine is a non-metal which is liquid at room temperature.

(ii) Mercury is the only metal that is liquid at room temperature.

(iii) Gallium (m.pt. 29.8ºC), caesium (m.pt. 28.5ºC) and francium (m.pt. 27ºC) are metals having low melting points.

(iv) Tungsten (W) has the highest melting point (3380ºC) among metals.

(v) Carbon has the highest melting point (4100ºC) among non-metals.

(vi) Oxygen is the most abundant element on the earth.

(vii) Aluminium is the most abundant metal.

(viii) Iron is the most abundant transition metal.

(ix) Highest density is shown by osmium (22.57 g cm^{-3}) or iridium (22.61 g cm^{-3}).

(x) Lithium is the lightest metal. Its density is 0.54 g cm^{-3}.

(xi) Silver is the best conductor of electricity.

(xii) Diamond (carbon) is the hardest natural substance.

(xiii) Francium has the highest atomic volume.

(xiv) Boron has the lowest atomic volume.

(xv) The most abundant gas in atmosphere is nitrogen.

(xvi) Fluorine is the most electronegative element.

(xvii) Chlorine has the maximum negative electron gain enthalpy.

(xviii) Helium has the maximum ionisation enthalpy.

(xix) Cesium or francium has the lowest ionisation enthalpy.

(xx) Helium and francium are smallest and largest atoms respectively.

(xxi) H^- and I^- ions are the smallest and largest anions respectively.

(xxii) H^+ and Cs^+ ions are the smallest and largest cations respectively.

(xxiii) Cesium is the most electropositive element.

(xxiv) Element kept in water is phosphorus, P_4 (white or yellow).

(xxv) Element kept in kerosene are Na, K, Rb, Cs, etc.

(xxvi) Iodine is the element which sublimes.

(xxvii) Hydrogen is the most abundant element in the universe.

(xxviii) Only ozone is the coloured gas with garlic smell.

(xxix) Metalloids have electronegativity values closer to 2.0.

(xxx) First synthetic (i.e., man-made) element is technetium (At. No. 43).

(xxxi) Most poisonous metal-Plutonium.

(xxxii) Rarest element in earth's crust-Astatine.

(xxxiii) The elements coming after uranium are called transuranic elements. The elements with Z = 104 – 112, 114 and 116 are called trans-actinides or super heavy elements. All these elements are synthetic, i.e., man-made elements. These are radioactive elements and not found in nature.

(xxxiv) The elements ruthenium (Ru), germanium (Ge), polonium (Po) and americium (Am) were named in honour of the countries named **Ruthenia (Russia), Germany, Poland** and **America,** respectively.

(xxxv) The members of the actinide series are radioactive and majority of them are not found in nature.

(xxxvi) The element rutherfordium (Rf, 104) is also called Kurchatovium (Ku) and element dubnium (Db, 105), is also called hahnium.

(xxxvii) Promethium (Pm, 61) a member of lanthanide series is not found in nature. It is a synthetic element.

(xxxviii) Special names are given to the members of these groups in periodic table.

Group 1	or	IA	Alkali metals
Group 2	or	IIA	Alkaline earth metals
Group 15	or	VA	Pnicogens
Group 16	or	VIA	Chalcogens
Group 17	or	VIIA	Halogens
Group 18	or	VIIIA (zero)	Inert or noble gases

CHEMICAL BONDING

1. INTRODUCTION

Atoms are usually not capable of free existence but groups of atoms of the same or different elements exist as one species, e.g., H_2, O_2, P_4, S_8, H_2O.

A group of atoms existing together as one species and having characteristic properties is called a molecule.

Obviously, there must be some force which holds these atoms together within the molecules.

2. CHEMICAL BOND

This force which holds the atoms together within a molecule is caled a chemical bond.

2.1 Why do atoms combine ?

Lewis-Kossel Approach to Chemical Bonding

The atoms of different elements combine with each other in order to complete their respective octets (i.e., 8 electrons in their outermost shell) or duplet (i.e., outermost shell having 2 electrons) in case of H, Li and Be to attain stable nearest noble gas configuration.

2.2 Modes of Chemical Composition

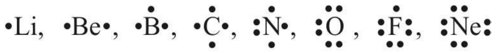
This can occur in two ways :

1. By complete transference of one or more electrons from one atom to another. This process is referred to as electrovalency and the chemical bond formed is termed as electrovalent bond or ionic bond.
2. By sharing of electrons. This can occur in two ways as follows :
   (a) When the shared electrons are contributed by the two combining atoms equally, the bond formed is called covalent bond.
   (b) When these electrons are contributed entirely by one of the atoms but shared by both, the bond formed is known as a coordinate bond, also called dative bond.

3. LEWIS SYMBOLS

In the formation of a molecule, only the outer shell electrons are involved and they are known as valence electrons. The inner shell electrons are well protected and are generally not involved in the combination process. It is, therefore, quite reasonable to consider the outer shell electrons, i.e., valence shell electrons while discussing chemical bonds.

G.N. Lewis introduced simple symbols to denote the valence shell electrons in an atom. The outer shell electrons are shown as dots surrounding the symbol of the atom. These symbols are known as Lewis symbols or electron dot symbols. These symbols ignore the inner shell electrons. A few examples are given below :



4. IONIC BOND

When a bond is formed by complete transference of electrons from one atom to another so as to complete their outermost orbits by acquiring 8 electrons (i.e., octet) or 2 electrons (i.e., duplet) in case of hydrogen, lithium etc. and hence acquire the stable nearest noble gas configuration, the bond formed is called ionic bond or electrovalent bond.

4.1 Explanation of Ionic Bond

Atoms are electrically neutral. Therefore, they possess equal number of protons and electrons. On losing an electron, an atom becomes positively charged since now the number of protons exceeds the number of electrons.

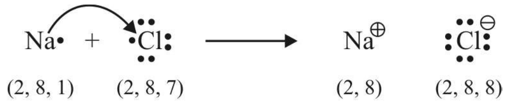
$$A \longrightarrow A^+ + e^-$$

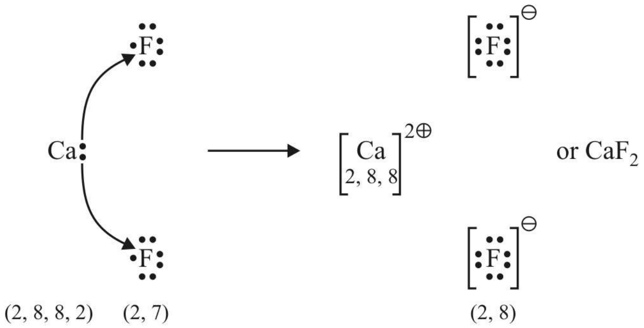
On the other hand, in case of atom, gaining the electron, the number of electrons exceeds the number of protons and thus the atom becomes negatively charged.

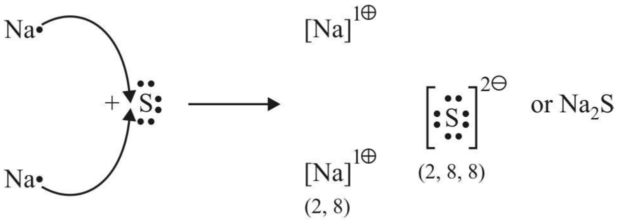
$$B + e^- \longrightarrow B^-$$

The oppositely charged particles formed above attract each other by electrostatic forces of attraction. The bond thus formed is known as electrovalent or ionic bond.

Examples







4.2 Electrovalency

The number of electrons lost or gained during the formation of an electrovalent linkage is termed as the electrovalency of the element.

For example, sodium and calcium lost 1 and 2 electrons respectively and so their valencies are 1 and 2. Similarly, chlorine and oxygen gain 1 and 2 electrons respectively, so they possess an electrovalency of 1 and 2. In other words, valency is equal to the charge on the ion.

4.3 Factors governing the formation of ionic bonds

(i) Ionisation Enthalpy (Ionization Energy)

Ionisation enthaly of any element is the amount of energy required to remove an electron from the outermost shell of an isolated atom in gaseous phase so as to convert it into a gaseous positive ion.

It is clear that lesser the ionisation enthalpy, easier will be the removal of an electron, i.e., formation of a positive ion and hence greater the chances of formation of an ionic bond. Ionisation enthalpy (I.E.) of alkali metals (i.e., group I elements) is low, hence they have more tendency to form positive ions.

(ii) Electron Gain Enthalpy (Electron Affinity)

Electron affinity or Electron gain enthalpy of an element is the enthalpy change that takes place when an extra electron is added to an isolated atom in the gaseous phase to form a gaseous negative ion.

Higher is the electron affinity, more is the energy released and stabler will be the negative ion produced. Consequently, the probability of formation of ionic bond will be enhanced. Halogens possess high electron affinity. So the formation of their negative ions is very common, e.g., in case of chlorine, electron affinity is +348 kJ/mole, i.e.,

$Cl\ (g) + e^- \rightarrow Cl^- + 348\ kJ/mole$

or $E.Z. = +348\ kJ\ mol^{-1}$

(iii) Lattice Enthalpy (Lattice Energy)

In the formation of ionic compounds, the positively charged ions combine with negatively charged ions to form the compound.

$A^+\ (g) + B^-\ (g) \rightarrow A^+ B^-\ (s)$

The energy released when the requisite number of gaseous positive and negative ions combine to form one mole of the ionic compound is called lattice enthaly.

4.4 Characteristics of Ionic Compounds

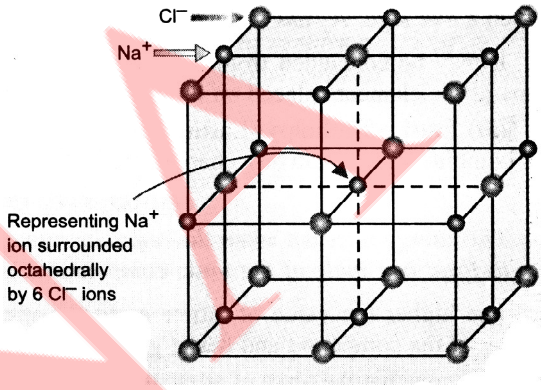
1. Physical State

These compounds usually exist in the solid state.

2. Crystal Structure

X-ray analysis of the ionic compounds shows that they exist as ions and not as molecules. These ions are arranged in a regular pattern in the three dimensional space to form a lattice.

The pattern of arrangement, however, depends upon the size and charges of the ions. For example, in case of sodium chloride, each sodium ion is surrounded by six chloride ions and each chloride by six sodium ions, thus giving rise to a three dimensional octahedral crystal structure (figure). The formula of an ionic compound merely indicates the relative number of ions present.



Crystal structure of NaCl

3. High melting and boiling points

Ionic compounds possess high melting and boiling points. This is because ions are tightly held together by strong electrostatic forces of attraction and hence a huge amount of energy is required to break the crystal lattice.

4. Solubility

Electrovalent compounds are soluble in solvents like water which are polar in nature and have high dielectric constant. It is due to the reason that the polar solvent interacts with the ions of the crystals and further the high dielectric constant of the solvent (i.e., capacity of the solvent to weaken the forces of attraction) cuts off the force of attraction between these ions. Furthermore, the ions may combine with the solvent to liberate energy called the hydration enthalpy which is sufficient to overcome the attractive forces between the ions.

Non-polar solvents like carbon tetrachloride, benzene etc. having low dielectric constants are not capable of dissolving ionic solids. Hence, ionic solids are soluble in polar solvents and insoluble in non-polar solvents.

5. Electrical conductivity

Ionic compounds are good conductors of electricity in solution or in the molten state. In solution or molten state, their ions are free to move. As the ions are charged, they are attracted towards electrodes and thus act as carriers of electric current.

6. Ionic Reactions

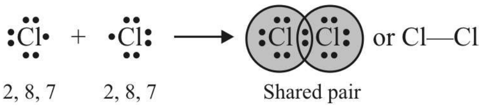
The reactions of the ionic compounds are, in fact, the reactions between the ions produced in solution. As the oppositely charged ions combine quickly, these reactions are, therefore, quite fast.

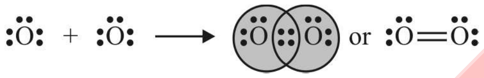
[e.g. $Na^+Cl^-(aq) + Ag^+NO_3^-(aq) \rightarrow AgCl(s) + NaNO_3(aq)$]

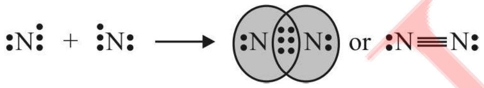
5. COVALENT BOND

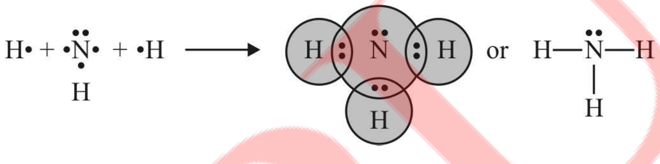
The bond formed between the two atoms by mutual sharing of electrons between them so as to complete their octets or duplets in case of elements having only one shell is called covalent bond or covalent linkage and the number of electrons contributed by each atom is known as covalency.

Example









Example

Draw the Lewis dot structure of HCN molecule.

Sol. **Step-1 :** Total number of valence electrons in HCN = 1 + 4 + 5 = 10 ($_1H = 1$, $_6C = 2, 4$, $_7N = 2, 5$)

Step-2 : Skeletal structure is HCN (C is least electronegative).

Step-3 : Putting one shared pair of electrons between H and C and one between C and N, and the remaining as lone pairs, we have

In this structure, duplet of H is complete but octets of C and N are not complete. Hence, multiple bonding is required between and N. Octets of C and N will be complete if there is triple bond between C and N. Thus,

Example

Draw the Lewis dot structure of CO_3^{2-} ion.

Sol. **Step-1 :** Total number of valence electrons of CO_3

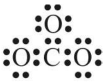
$= 4 + 3 \times 6 = 22$ ($_6C = 2, 4$, $_8O = 2, 6$)

Step-2 : Total number of electrons to be distributed in CO_3^{2-}

$= 22 + 2$ (for two units -ve charge) $= 24$

Step-3 : The skeletal structure of CO_3 is

Step-4 : Putting one shared pair of electrons between each C and O and completing the octets of oxygen, we have



In this structure, octet of C is not complete. Hence, multiple bonding is required between C and one of the O–atoms. Drawing a double bond between C and one O-atom serves the purpose :

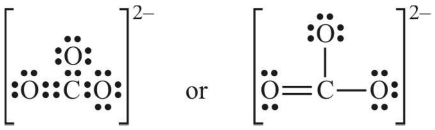


Table : Lewis structures of some typical molecules and ions

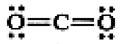
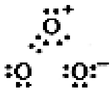
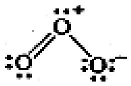
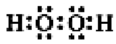
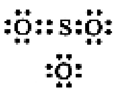
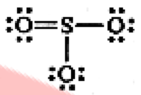
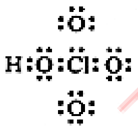
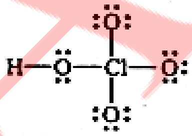
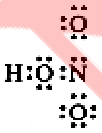
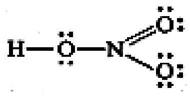
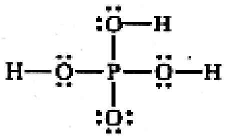
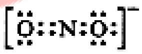
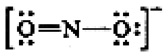
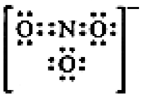
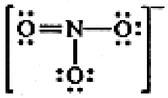
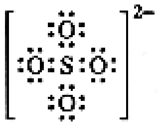
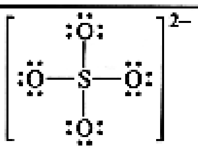
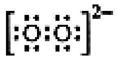
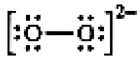
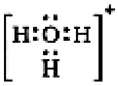
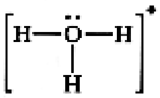
Molecule/ Ion		Lewis Representation		
(i)	CO		or	
(ii)	CO_2		or	
(iii)	O_2		or	
(iv)	O_3		or	
(v)	H_2O_2		or	
(vi)	SO_3		or	
(vii)	$HClO_4$ (Perchloric acid)		or	
(viii)	HNO_2 (Nitrous acid)		or	
(ix)	HNO_3 (Nitric acid)		or	
(x)	H_3PO_4 (Phosphoric acid)		or	
(xi)	CN^- (Cyanide ion)		or	
(xii)	NO_2^- (Nitrite ion)		or	
(xiii)	NO_3^- (Nitrate ion)		or	

Table : Lewis structures of some typical molecules and ions

Molecule/ Ion		Lewis Representation		
(xiv)	SO_4^{2-} (Sulphate ion)		or	
(xv)	O_2^{2-} (Peroxide ion)		or	
(xvi)	H_3O^+ (Hydronium ion)		or	

6. FORMAL CHARGE

The formal charge on an atom in a molecule or ion is defined as the difference between the number of valence electrons of that atom in the free state and the number of electrons assigned to that atom in the Lewis structure, assuming that in each shared pair of electrons, the atom has one electron of its own and the lone pair on it belongs to it completely. Thus, it can be calculated as follows :

$$\begin{bmatrix}\text{Formal charge (F.C.) on} \\ \text{an atom in a molecule / ion}\end{bmatrix} = \begin{bmatrix}\text{Total no. of valence electrons} \\ \text{in the free atom}\end{bmatrix} -$$

$$\begin{bmatrix}\text{Total no. of electrons of} \\ \text{lone pairs (non – bonding electrons)}\end{bmatrix} - \frac{1}{}$$

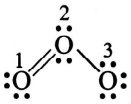
$$\begin{bmatrix}\text{Total no. of shared electrons} \\ \text{(bonding electrons)}\end{bmatrix}$$

i.e., $FC = V - L - \frac{1}{}S$

Example

Calculate formal charge on each O-atom of O_3 molecule.

Sol. Lewis structure of O_3 is :



The atoms have been numbered as 1, 2 and 3.

Formal charge on end O-atom numbered 1

$$= 6 - 4 - \frac{1}{}(4) = 0$$

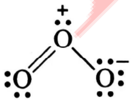
Formal charge on central O-atom numbered 2

$$= 6 - \quad - \frac{1}{}(6) = +1$$

Formal charge on end O-atom numbered 3

$$= 6 - 6 - \frac{1}{}(2) = -1$$

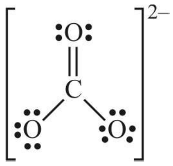
Hence, we represent O_3 along with formal charges as :



Example

Write the formal charges on atoms in (i) carbonate ion (ii) nitrite ion.

Sol. (i) Lewis structure of CO_3^{2-} ion is



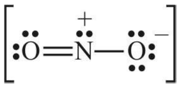
Formal charge on C atom $= 4 - 0 - \frac{1}{}(8) = 0,$

Formal charge on double bonded O atom

$$= 6 - 4 - \frac{1}{}(4) = 0$$

Formal charge on single bonded O atom

$$= 6 - 6 - \frac{1}{}(\quad) = -1$$

(ii) Lewis structure of NO_2^- ion is 

Formal charge on N atom

$$= 5 - \quad - \frac{1}{}(6) = 0,$$

Formal charge on double bonded O atom

$$= 6 - 4 - \frac{1}{}(4) = 0$$

Formal charge on single bonded O atom

$$= 6 - 6 - \frac{1}{}(\quad) = -1$$

Significance of formal charge. The main advantage of the calculation of formal charges is that it helps to select the most stable structure, i.e., the one with least energy out of the different possible Lewis structures. The most stable is the one which has the smallest formal charges on the atoms.

7. LIMITATIONS OF LEWIS-LANGMUIR CONCEPT OF COVALENT BOND

Lewis-Langmuir concept of covalent bond, as explained in ec. 4.8, has the following limitations :

(i) It could not explain how the atoms are held together in the molecules like H_2, Cl_2 etc. in which there are no ions and hence there are no electrostatic forces of attraction, i.e., it could not explain the formation of a covalent bond.

(ii) It could not explain the shapes of molecules containing covalent bonds.

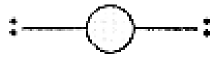
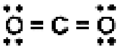
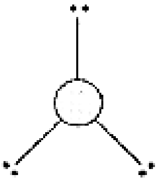
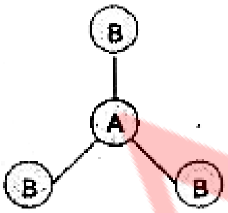
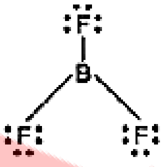
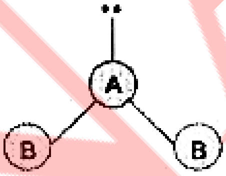
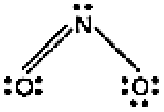
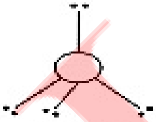
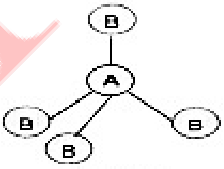
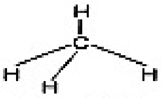
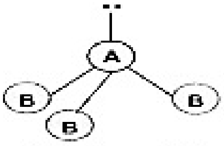
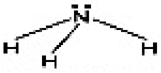
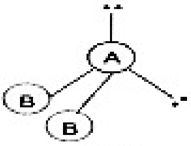
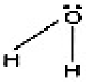
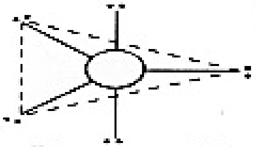
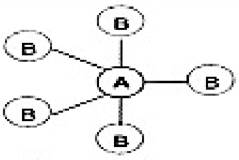
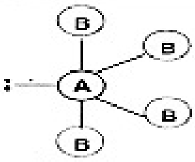
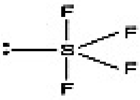
(iii) It could not explain the release of energy during the formation of a covalent bond.

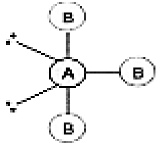
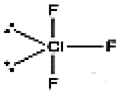
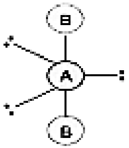
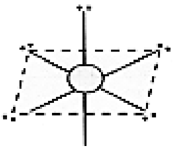
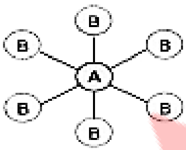
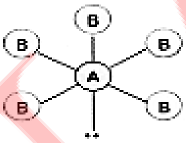
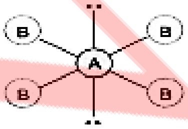
8. VALENC SHEELL ELECTRON PAIR REPULSION THEORY

The first simple theory that was put forward to explain the shapes of molecules is known as Valence Shell. Electron Pair Repulsion (VSEPR) theory. This theory was given by Sidgwick and Powell in 1940 and was further improved by Nyholm and Gillespie in 1957.

The electron pairs surrounding the central atom repel one another and move so far apart from one another that there are no further repulsions between them. As a result, the molecule has minimum energy and maximum stability.

Table : Shapes (Geometry) of molecules containing bond pairs only or bond pairs and lone pairs

Total No. of electron pairs	Geometry of the electron pairs	Bond pairs	Lone pairs	(Molecular Formula)	Geometry (Shape) of the molecule	Illustrative Example (Other Examples)
2	 Linear	2	0	(AB_2)	 Linear	 (BeF_2, $BeCl_2$, $HgCl_2$)
3	 Triangular planar	3	0	(AB_3)	 Triangular planar	 ($AlCl_3$, SO_3)
		2	1	(AB_2L)	 Bent (V-shape)	 (SO_2, O_3, $SnCl_2$)
4	 Tetrahedral	4	0	(AB_4)	 Tetrahedral	 (SiF_4, NH_4^+)
		3	1	(AB_3L)	 Trigonal pyramidal	 (PCl_3, NCl_3,NF_3, PH_3, H_3O^+)
		2	2	(AB_2L_2)	 Bent	 (H_2S, NH_2^-)
5	 Trigonal bipyramidal	5	0	(AB_5)	 Trigonal bipyramidal	PCl_5 (PF_5, $SbCl_5$, AsF_5)
		4	1	(AB_4L)	 See saw	 (SF_4)

		3 (AB_3L_2)	2	 T-shaped	 (ClF_3)
		2 (AB_2L_3)	3	 Linear	XeF_2 (I_3^-, Br_3^-, ICl_2^-)
6	 Octahedral	6 (AB_6)	0	 Octahedral	SF_6
		5 (AB_5L)	1	 Square pyramidal	ClF_5 (IF_5, BrF_5)
		4 (AB_4L_2)	2	 Square planar	XeF_4

8.1 Calculation of total number of electron pairs, bond pairs and lone pairs and predicting the shapes of the molecules and ions.

(i) Total no. of electron pairs around the central atom

$= \frac{1}{}$ (No. of valence electrons of central atom +

No. of atoms linked to central atom by single bonds)

For negative ions, add number of electrons equal to the units of negative charge on the ion to the valence electrons of the central atom.

For positive ions, subtract number of electrons equal to the units of positive charge on the ion from the valence electrons of the central atom.

(ii) No. of bond pairs (shared pairs) = No. of atoms linked to central atom by single bonds.

(iii) No. of lone pairs = Total no. of electron pairs – No. of shared pairs.

Example

On the basis of VSEPR theory, predict the shapes of the following :

(i) ClF_3 **(ii) BrF_5**

Sol. (i) Shape of ClF_3

No. of valence electrons of the central Cl atom = 7

No. of atoms linked to it by single bonds = 3.

∴ Total no. of electron pairs around $Cl = \frac{7+3}{} = 5$

No. of bond pairs = No. of atoms linked to Cl = 3.

∴ No. of lone pairs = 5 – 3 = 2.

Thus, the molecule is of the type AB_3L_2.

Hence, it is T-shaped.

(ii) Shape of BrF_5

No. of valence electrons of central Br atom = 7

No. of atoms linked to it by single bonds = 5.

∴ Total no. of electron pairs around $Br = \frac{7+5}{} = 6$

No. of bond pairs = No. of atoms linked to Br = 5.

∴ No. of lone pairs = 6 – 5 = 1.

Thus, the molecule is of the type AB_5L. Hence, it has square pyramidal shape.

9. HYBRIDISATION

Hybridisation is defined as the mixing of the atomic orbitals belonging to the same atom but having slightly different energies so that a redistribution of energy takes place between them resulting in the formation of new orbitals of equal energies and identical shapes. The new orbitals thus formed are known as hybrid orbitals.

Some Important Points about Hybridisation

(i) Only those orbitals which have approximately equal energies and belong to the same atom or ion can undergo hybridisation.

(ii) Number of hybrid orbitals produced is equal to the number of atomic orbitals mixed.

(iii) It is not necessary that all the half-filled orbitals must participate in hybridisation. Similarly, it is not necessary that only half-filled orbitals should participate in hybridisation. Even completely filled orbitals with slightly different energies can also participate.

(iv) Hybridisation never takes place in isolated atoms but it occurs only at the time of bond formation.

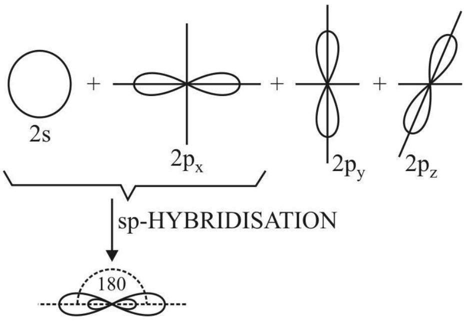
(v) Type of hybridisation indicates the geometry of molecules. One can tell the shape of a molecule by knowing the kind of hybridisation involved.

(vi) The bigger lobe of the hybrid orbital always has +ve sign while the smaller lobe on the opposite side has a -ve sign.

9.1 Type of Hybridisation

1. Diagonal or sp hybridisation

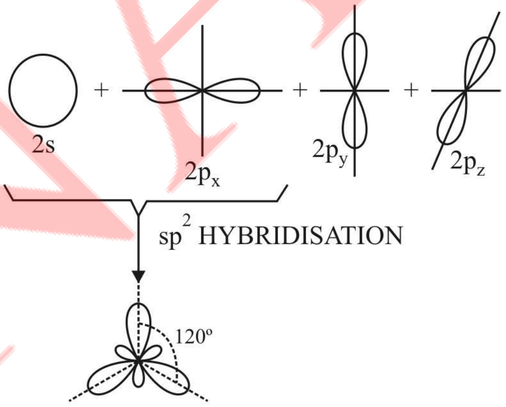
When one s and one p orbital belonging to the same main shell of an atom mix together to form two new equivalent orbitals, the type of hybridisation is called sp hybridisation or diagonal hybridisation. The new orbitals formed are called sp hybrid orbitals.



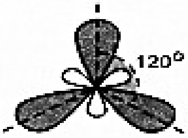
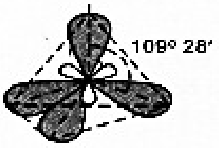
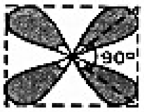
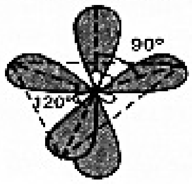
TWO sp-HYBRID ORBITALS

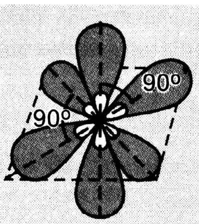
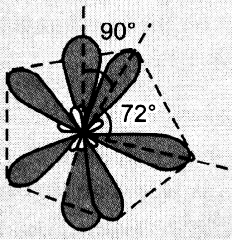
2. Trigonal or sp^2 hybridisation

When one s and two p orbitals of the same shell of an atom mix to form three new equivalent orbitals, the type of hybridisation is called sp^2 hybridisation or trigonal hybridisation. The new orbitals formed are called sp^2 hybrid orbitals.



THREE sp^2 HYBRID ORBITALS

Types of Hybridisation	Atomic orbitals Involved	Representing directions of hybrid orbitals formed along with bond angles	Shape of the molecule	Examples
1. *sp*	one *s* + one *p*		Linear	$BeCl_2$, BeH_2 C_2H_2, $HgCl_2$
2. *sp*^{2}	one *s* + two *p*		Triangular planar	BF_3, BCl_3, C_2H_4, NO_3^- CO_3^{2-}
3. *sp*^{3}	one *s* + three *p*		Tetrahedral	CH_4, CCl_4, $SnCl_4$, NH_4^+
4. *dsp*^{2}	one *d* ($d_{x^2-y^2}$) +one *s* + two *p*		Square planar	$[Ni(CN)_4]^{2-}$, $[Pt\,Cl_4]^{2-}$
5. *sp*^{3}*d*	one *s* + three *p* + one *d* (d_{z^2})		Trigonal bipyramidal	PF_5, PCl_5

Types of Hybridisation	Atomic orbitals involved	Representing directions of hybrid orbitals formed along with bond angles	Shape of the molecule	Examples
6. sp^3d^2 or d^2sp^3	one s + three p +two d ($d_{x^2-y^2}$ and d_{z^2})		Octahedral	SF_6, $[CrF_6]^{3-}$, $[Co(NH_3)_6]^{3+}$
7. sp^3d^3	one s + three p + d_{xy}, d_{yz}, d_{xz}		Pentagonal bipyramidal	IF_7

9.2 Predicting Hybridisation

(a) Predicting hybridisation

Calculate the number of hybrid orbitals (X) to be formed by the central atom as follows :

$$X = \frac{1}{2}\left[\left\{\begin{matrix}\text{No. of valence electrons}\\ \text{of the central atom}\end{matrix}\right\} + \left\{\begin{matrix}\text{No. of monovalen atoms / groups}\\ \text{surrounding the central atom}\end{matrix}\right\} - \left\{\begin{matrix}\text{Charge on the cation}\\ \text{if the given species is}\\ \text{a polyatomic cation}\end{matrix}\right\} + \left\{\begin{matrix}\text{Charge on the anion}\\ \text{if the given species is}\\ \text{a polyatomic anion}\end{matrix}\right\}\right]$$

i.e., $X = \frac{1}{2}[VE + MA - c + a]$

Note that only monovalent atoms (MA) or groups are to be considered. For divalent ions, MA = 0.

If X = 2, it means two hybrid orbitals are to be formed. Hence, hybridization is sp. If X = 3, it means three hybrid orbitals are to be formed. Hence, hybridisation is sp^2 and so on, as given in the following table :

Value of X	2	3	4	5	6	7
Type of hybridisation	sp	sp^2	sp^3	sp^3d	sp^3d^2	sp^3d^3

10. VALENCE BOND THEORY

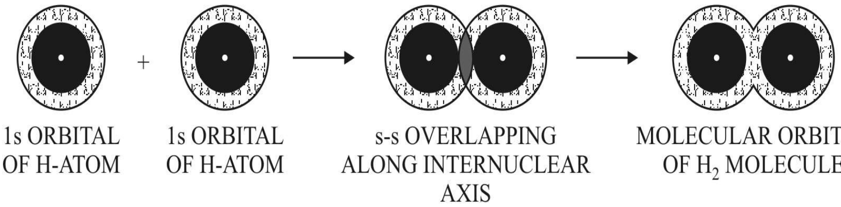
10.1 Types of covalent bond

Depending upon the type of overlapping, the covalent bonds are mainly of two types :

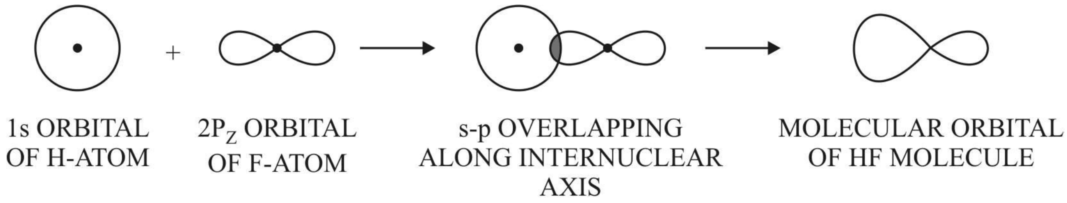
1. Sigma (σ) bond

When a bond is formed between two atoms by the overlap of their atomic orbitals along the internuclear axis (end to end or head on overlap), the bond formed is called sigma (σ) bond.

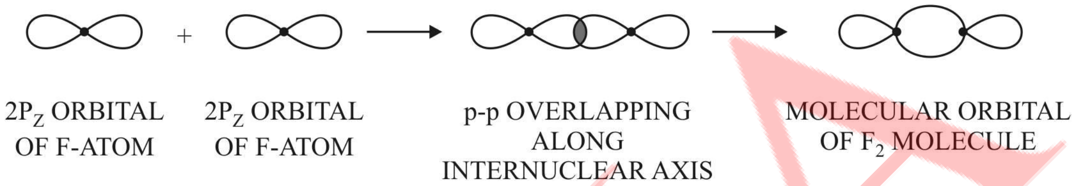
(i) s-s overlapping



(ii) s-p overlapping

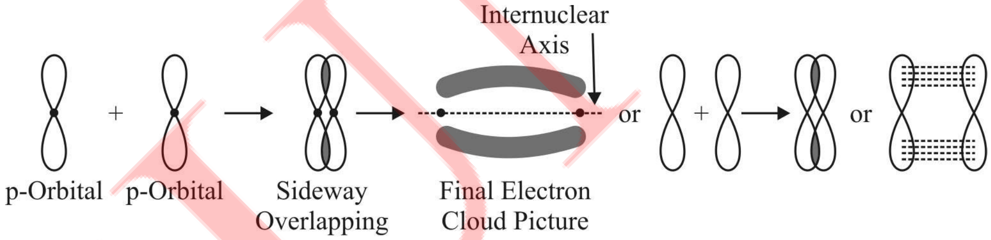


(iii) p-p overlapping



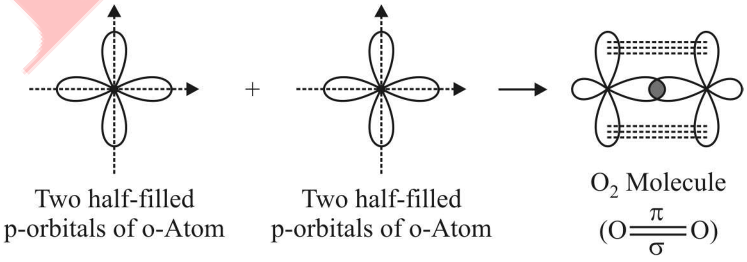
2. Pi (π) Bond

Pi-bond is formed by lateral (sideways) overlapping of p-orbitals, i.e., by overlapping of p-orbitals in a direction at right angles to the internuclear axis (figure).



p-p overlapping forming a pi bond

(i) In case of oxygen molecule (each oxygen atom having electronic configuration, $1s^2\, 2s^2\, 2p_x^2\, 2p_y^1\, 2p_z^1$), the two atoms are held together by one σ-bond and one π-bond as shown in figure.



Formation of oxygen molecule

Table : Comparison and sigma and pi bonds

Sigma (σ) Bond	Pi (π) Bond
(i) This bond is formed by overlap of orbitals along their internuclear axis (end to end overlap).	(i) This is formed by sideway overlapping of orbitals (lateral overlapping).
(ii) This is formed by overlapping between s-s, s-p or p-p orbitals.	(ii) This is formed by the overlap of p-p orbitals only.
(iii) Overlapping is quite large and hence sigma bond is a strong bond.	(iii) Overlapping is to a small extent. Hence, π-bond is a weak bond.
(iv) Electron cloud in this case is symmetrical about the line joining the two nuclei.	(iv) Electron cloud of π-bond is unsymmetrical.
(v) Sigma bond consists of only one electron cloud, symmetrical about the internuclear axis.	(v) Pi (π) bond consists of two electron clouds, one above the plane of atomic nuclei and the other below it.
(vi) Free rotation about a σ-bond is possible.	(vi) Free rotation about a π-bond is not possible because on rotation, overlapping vanishes and so the bond breaks.

10.2 Bond Parameters

10.2.1 Bond length

The equilibrium distance between the centres of the nuclei of the two bonded atoms is called its bond length.

10.2.1.1 Factors affecting bond length

(i) Size of the atoms : The bond length increases with increase in the size of the atoms. For example, bond lengths of H–X are in the order :

HI > HBr > HCl > HF

(ii) Multiplicity of bond : The bond length decreases with the multiplicity of the bond. Thus, bond length of carbon-carbon bonds are in the order :

$C\equiv C < C=C < C-C$

(iii) Type of hybridisation (discussed later in sec. 4.24). As an s-orbital is smaller in size, greater the s-character, shorter is the hybrid orbital and hence shorter is the bond length. For example,

Bond lengths :	sp^3 C–H >	sp^2 C–H >	sp C–H
s-character :	(25%)	(33%)	(50%)

10.2.2 Bond energy

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 simply bond enthalpy.

10.2.2.1 Factors affecting Bond energy

(i) Size of the atoms : Greater the size of the atoms, greater is the bond length and less is the bond dissociation enthalpy, i.e., less is the bond strength.

(ii) Multiplicity of bonds : For the bond between the same two atoms, greater is the multiplicity of the bond, greater is the bond dissociation enthalpy. This is firstly because atoms come closer and secondly, the number of bonds to be broken is more. For example, bond dissociation enthalpies of H_2, O_2 and N_2 are in the order :

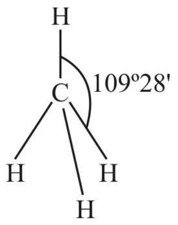
$H-H < O=O < N\equiv N$

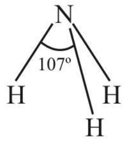
(iii) Number of lone pairs of electrons present : Greater the number of lone pairs of electrons present on the bonded atoms greater is the repulsion between the atoms and hence less is the bond dissociation enthalpy. For example, for a few single bonds, we have

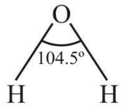
Bond	C–C (in H_3C-CH_3)	N–N (in $:N\equiv N:$)	O–O (in $:\ddot{O}-\ddot{O}:$)	F–F ($:\underset{..}{\ddot{F}}-\underset{..}{\ddot{F}}:$)
Lone pairs of electrons on each atom	0	1	2	3
Bond enthalpy (kJ mol^{-1})	348	163	146	139

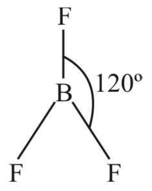
10.2.3 Bond angle

The angle between the lines representing the directions of the bonds, i.e., the orbitals containing the bonding electrons is called the bond angle.









10.2.4 Bond order

In the Lewis representation of a molecule or ion, the number of bonds present between two atoms is called bond order. For example, the bond orders of a few molecules are given below :

Molecule :	H—H	O=O	N≡N	C≡O
Bond order :	1	2	3	3

For odd electron molecules, as the three electron bond is considered as equivalent to half covalent bond, bond order can be fractional also. For example, Lewis structure of NO is

$:N\overset{\cdot\cdot\cdot}{=}O:.$

11. MOLECULAR ORBITAL THEORY

There is another approach to chemical bonding known as molecular orbital theory (MOT) developed by **Mulliken** (1932) and **Hund**, which explains the bonding characteristics in a better way. The molecular orbital theory considers the entire molecule as a unit with all the electrons moving under the influence of all the nuclei present in the molecular. This approach recognizes that each electron belongs to the molecule as a whole and may move within the entire molecule.

11.1 Molecular Orbitals

When the atoms to be bonded come close together, the orbitals of the bonded atoms lose their individual character and fuse (overlap) to form larger orbitals called molecular orbitals. Like atomic orbitals, there are molecular orbitals in a molecule. The only difference is that in atomic orbitals, electrons move under the influence of only one nucleus (i.e. Atomic orbital are monocentric), while in molecular orbitals, electrons move under the influence of many nuclei, they are polycentric.

11.2 Important features of M.O.T.

(i) Like an Atomic orbital which is around the nucleus of an atom there are molecular orbital which are around the nuclei of a molecule.

(ii) The molecular orbitals are entirely different from the atomic orbitals from which they are formed.

(iii) The valence electrons of the constituent atoms are considered to be moving under the influence of nuclei of participating atoms in the molecular orbital.

(iv) The molecular orbitals possess different energy levels like atomic orbitals in an isolated atom.

(v) The shape of molecular orbitals are dependent upon the shapes of atomic orbitals from which they are formed.

(vi) Molecular orbitals are arranged in order of increasing energy just like atomic orbitals.

(vii) The number of molecular orbitals formed is equal to the number of atomic orbitals combining in bond formation.

(viii) Like atomic orbitals, the filling of electrons in molecular orbitals is governed by the three principles such as **Aufbau principle, Hund's rule and Pauli's exclusion principle.**

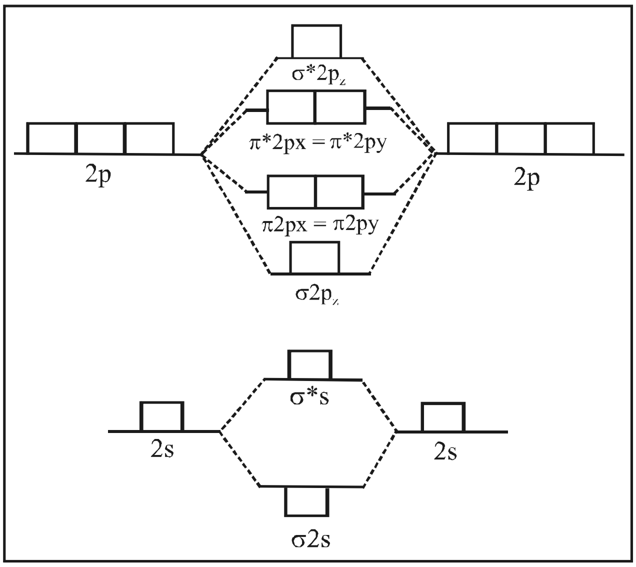
11.3 Conditions for atomic orbitals to form M.O.

(i) The combining A.O. should be of a comparable energy.

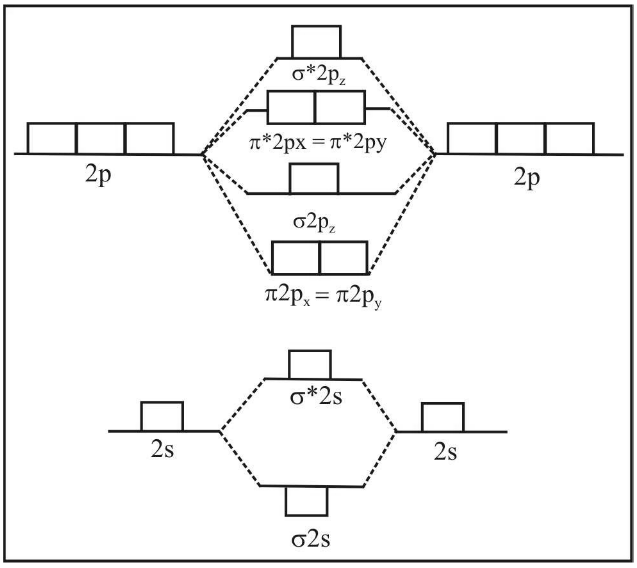
(ii) The combining atomic orbitals must overlap to a large extent greater the overlap, stable is the molecule formed.

11.4 Relative energies of M.O. and filling of electron

Energy diagram is shown below



M.O Energy level diagram for O_2, F_2 and Ne.



M.O energy diagram for Li_2, Be_2, B_2, C_2 and N_2 molecule

12. METALLIC BOND

The constituent particles of metallic solids are metal atoms which are held together by metallic bond. A metal atom is supposed to consit of two parts, valence electrons and the remaining part (the neucleus and the inner shells) called **kernel.** The kernels of metal atoms occupy the lattice sites while the space between the kernel is occupied by valence electrons. Due to small ionisation energy the valence electrons of metal atoms are not held by the nucleus firmly. Therefore, the electrons leave the field of influence of one kernel and come under the influence of another kernel. Thus the electrons are not localised but are mobile. The simultaneous attraction between the kernels and the mobile electrons which hold the kernel together is known as **metallic bond.** This model is known electron sea model.

13. HYDROGEN BONDING

When a hydrogen atom linked to a highly electronegative atom (like F,O, or N) comes under the influence of another strongly electronegative atom, then a weak bond is developed between them which is called as **hydrogen bond.** It is represented by dotted line as follows

$$\overset{+\delta}{H}-\overset{+\delta}{X}\text{-----}\overset{+\delta}{H}-\overset{-\delta}{X}\text{-----}\overset{+\delta}{H}-\overset{-\delta}{X}$$

As a result of hydrogen bonding, a H–atom links the two electronegative atoms simultaneously, one by a covalent bond and the other by a hydrogen bond. Hence it is said to form a hydrogen bridge. It is merely a strong electrostatic attractive forces and not a normal chemical bond. It is very weak (strength about 2-10 K cal/mol).

13.1 Conditions for Hydrogen bonding

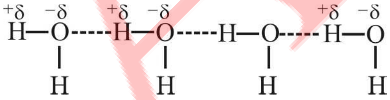
(a) The molecule must contain a highly electronegative atom linked to H-atom. The higher the electronegativity, more is the polarisation of the molecule.

(b) The size of the electronegative atom should be small. The smaller the size the greater is the electrostatic attraction.

13.2 Types of Hydrogen bonding

13.2.1 Intermolecular Hydrogen bonding

When hydrogen bonding takes place between different molecules of the same or different compounds, it is called intermolecular hydrogen bonding e.g. HF, H_2O, ROH (same compound) water-alcohol, water ammonia (different compound) etc.

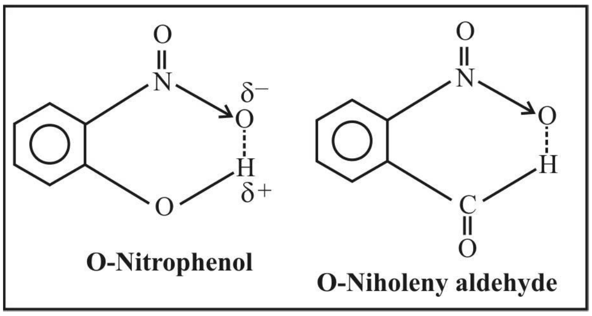


$$\overset{+\delta}{H}-\underset{\substack{|\\ H}}{\overset{-\delta}{O}}\text{-----}\overset{+\delta}{H}-\underset{\substack{|\\ H}}{\overset{-\delta}{O}}\text{-----}H-\underset{\substack{|\\ H}}{O}\text{-----}\overset{+\delta}{H}-\underset{\substack{|\\ H}}{\overset{-\delta}{O}}$$

13.2.2 Intramolecular hydrogen bonding

The hydrogen bonding which takes place within a molecule itself. It takes place in compounds containing two groups such that one group contain a H-atom linked to an electronegative atom and the other group contains a highly electronegative atom linked to a lesser electronegative atom. The bond is formed between the H-atom of one group with the more electronegative atom of the other group.

Examples are as shown below



O-Nitrophenol

O-Niholeny aldehyde

14. VANDER WAAL'S FORCES

(a) This type of attractive forces occurs in case of non polar molecules such as H_2, O_2, Cl_2, CH_4, CO_2, etc.

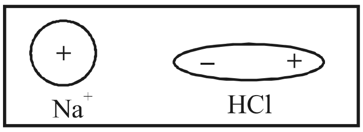
(b) The existence of weak attractive forces among the nonpolar molecule was first proposed by Dutch scientist **J.D. Vander Waal.**

(c) Vander waal force $\propto$ molecular weight

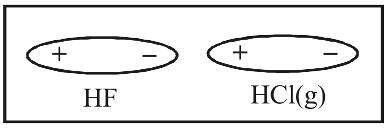
$\propto$ Boiling point

14.1 Types of Vander Waal's force

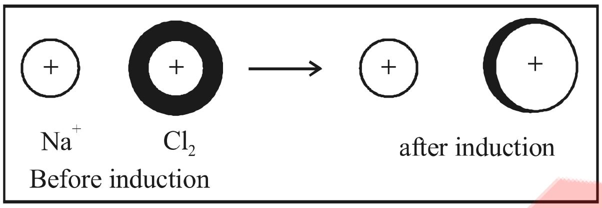
14.1.1 Ion dipole attraction - This force is between an ion such as Na^+ and a polar molecule such as HCl



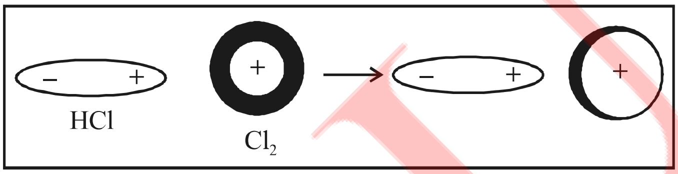
14.1.2 Dipole dipole attraction - It is again in between two polar molecules such as HF and HCl



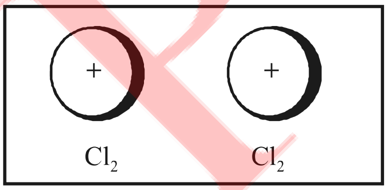
14.1.3 Ion induced dipole attraction - In this case a neutral molecule is induced by an ion as a dipole as shown in fig



14.1.4 Dipole - induced dipole attraction : In this case a neutral molecule is induced as a dipole by another dipole as show in fig



14.1.5 Induced dipole - induced dipole attraction or London dispersion force between two non polar molecules as in Cl_2, He etc.



NOTE

The relative strength of various bonds is as follows :

Ionic bond > Covalent bond > Metallic bond > H-bond > Vander waal bond.

15. DIPOLE MOMENT

A molecule with positive and negative charge centres in equilibrium is called as dipole and is characterised by possessing a quantity dipole moment (μ) defined as the product of the magnitude of charge (q) and the distance (d) separating the centres of +ve and –ve charges. Its direction is from +ve end to – ve end.

$$\mu = q \times d$$

The charge q on an electron is 4.8×10^{-10} esu. The distance is measured in cm and is of order of 1 Å, i.e., 10^{-8} cm. Its unit in CGS system is debye (D).

A molcule will have a dipole moment of 1 Debye (D) if charges of 1×10^{-8} esu are separated by a distance of 1Å.

Thus, $1D = 1 \times 10^{-18}$ esu. cm.

Applications of Dipole Moment

(i) The molecules having zero moment are non-polar molecules and those having $\mu_{net} \neq 0$ are polar in nature.

(ii) The value of dipole moment can be used for determining the amount of ionic character in a bond.

Percentage of ionic character

$$= \frac{\text{Experimental value of dipole moment}}{\text{Theoretical value of dipole moment}} \times 100$$

SOLVED EXAMPLES

Example - 1

Which of the following compounds has the largest dipole moment ?

(i) CH_3OH (ii) CH_4

(iii) CF_4 (iv) CO_2

(v) CH_3F.

Sol. CH_4 and CF_4 have tetrahedral structure and are symmetrical, hence their dipole moment is zero, CO_2 is linear and hence its dipole moment is also zero of the remaining CH_3OH and CH_3F, since F is more electronegative than O, CH_3F will have high dipole moment.

Example - 2

What type of bond is formed when atoms have

(i) Zero difference of electronegativity.

(ii) Little difference of electronegativity.

(iii) High difference of electronegativity.

Sol. (i) Non-polar covalent

(ii) Polar covalent

(iii) Electro-valent.

Example - 3

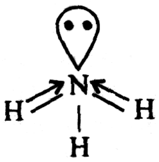
Explain the formation of a chemical bond.

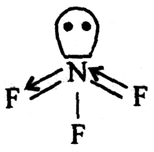
Sol. A chemical bond is formed by mutual sharing or by transfer of one or more electrons. In doing so, each combining atom acquires stable noble gas electronic configuration having 8 electrons in its outermost shell.

Example - 4

Why NH_3 has higher dipole moment than NF_3 ?

Sol. In NH_3 dipoles are towards lone pair whereas in NF_3 dipoles A are opposite to lone pair of electrons.





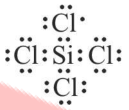
Example - 5

Draw the Lewis structures for the following molecules and ions :

H_2S, $SiCl_4$, BeF_2, CO_3^{2-}, HCOOH.

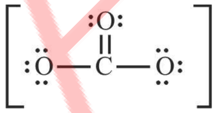
Ans. H_2S

$SiCl_4$

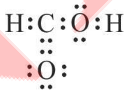


BeF_2

CO_3^{2-}



HCOOH



Example - 6

Write the favorable factors for the formation of ionic bond.

Sol. Factors which favour the formation of ionic bond :

(i) **Low ionisation energy :** In the formation of ionic bond a metal atom loses electron to form cation. This process requires energy equal to the ionisation energy. Lesser the value of ionisation, greater will be the tendency of the atom to form cation.

(ii) **High electron affinity :** The value of electron affinity gives the tendency of an atom to form anion. Greater the value of electron affinity, more will be the tendency of an atom to form anion.

(iii) **High lattice energy :** The lattice energy should be high so that it overcomes the apparent deficit of energy of absorption, that is, sublimation energy, ionization energy, dissociation energy and second affinity. Higher the lattice energy, greater will be the ease of formation of the ionic compound.

The magnitude of lattice energy gives an idea about the interionic forces. It depends upon the following factors :

(a) **Size of the ions :** Smaller the size of the ions, lesser is the inter-nuclear distance. Consequently, the interionic attractions will be high and the lattice energy will also be large.

(b) **Charge on the ions :** Larger the magnitude of charge on the ions, greater will be the attractive forces between the ions. Consequently, the lattice energy will be high.

Example - 7

Discuss the shape of the following molecules using the VSEPR model.

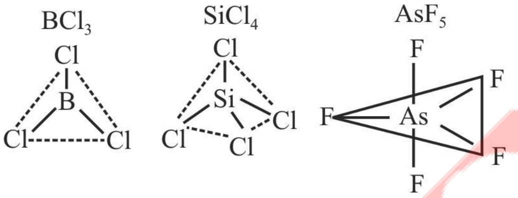
$BeCl_2$, BCl_3, $SiCl_4$, AsF_5, H_2S, PH_3.

Sol. **$BeCl_2$:** A linear molecule. Be atom has 2 electrons in it outermost orbit. Each chlorine atom has seven valence electrons. The Lewis structure of $BeCl_2$ is

$$\cdot Be \cdot + 2\,\cdot\ddot{\underset{..}{Cl}}: \longrightarrow :\ddot{\underset{..}{Cl}}\cdot\cdot Be\cdot\cdot\ddot{\underset{..}{Cl}}: \longrightarrow Cl–Be–Cl$$

There are two electrons pairs and to minimise the repulsion, these electron pairs tend to keep themselves far away from each other, i.e., 180° apart. This gives $BeCl_2$ a linear structure.

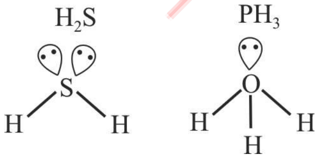
BCl_3 : In BCl_3 molecule, the three bond pairs of electrons are located around B in a triangular arrangement. Thus, the molecule BCl_3 has a **triangular planar geometry.**



$SiCl_4$: A tetrahedral molecule. Si has 4 electrons in its outermost shell. Due to mutual sharing of electrons with Cl there are 4 electron pairs around Si. To keep the repulsion at the minimum, these 4 electron pairs should be arranged in a tetrahedral manner around Si. Thus, $SiCl_4$ is a tetrahedral molecule.

AsF_5 : Trigonal bipyramidal molecule : As has five electrons in its outermost orbit. Due to sharing of 5 electrons from 5 F-atoms, there are in all 5 electron pairs. These are distributed in space to form a trigonal bypyramid.

H_2S : Bent (V-shaped) structure : S has 6 electrons its outermost shell. 2H-atoms contribute 2 electrons during bonding. Thus, there are 8 electrons or 4 electron pairs around S. This gives a tetrahedral distribution of electron pairs around S. The two corners of the tetrahedron are occupied by H-atoms and the other two by the lone-pairs of electrons. Thus, H_2S has a bent structure.

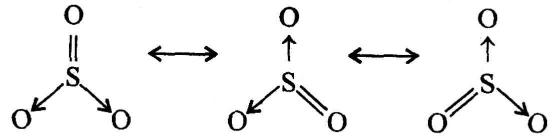


PH_3 : Trigonal pyramidal : Phosphorus atom has 5 electrons in its outermost orbit. H-atoms contribute one electron each to make in all 8 electrons around P-atom. Thus, 4 pairs of electrons would be distributed in a tetrahedral fashion around the central atom. Three pairs form three P-H bonds while the fourth pair remains unused. Due to repulsion between the bonding and lone pairs of electrons, the angle $H\hat{P}H$ is not exactly tetrahedral (109° 28′). The actual HPH angle is 93.3°. Thus PH_3 is a trigonal pyramidal molecule.

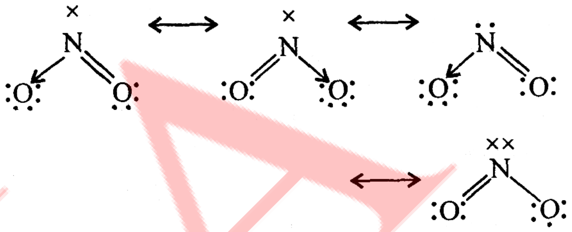
Example - 8

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

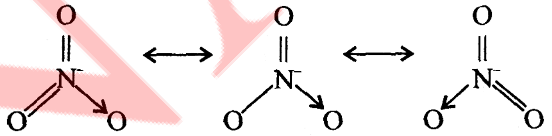
Sol. **(SO_3)**



(NO)



(NO_3^-)

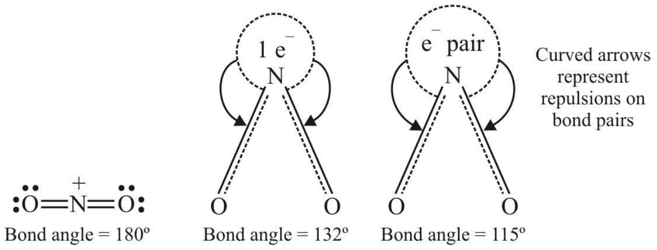


Example - 9

Arrange the following in order of decreasing bond angle, giving reason

NO_2, NO_2^+, NO_2^-

Ans. $NO_2^+ > NO_2 > NO_2^-$. This is because NO_2^+ has no lone pair of electrons (i.e. has only bond pairs on two sides) and hence it is linear. NO_2 has one unshared electron while NO_2^- has one unshared electron pair. There are greater repulsions on N–O bonds in case of NO_2^- than in case of NO_2.



Example - 10

Arrange the following in order of decreasing bond angles

(i) CH_4, NH_3, H_2O, BF_3, C_2H_2 (ii) NH_3, NH_2^-, NH_4^+

Sol. (i) C_2H_2(180°) > CH_4 (109° 28′) > BF_3 (120°) > NH_3 (107°) > H_2O > (104.5°)

(ii) $NH_4^+ > NH_3 > NH_2^-$

This is because all of them involve sp^3 hybridization. The number of lone pair of electrons present on N-atom are 0, 1 and 2 respectively. Greater the number of lone pairs, greater are the repulsions on the bond pairs and hence smaller is the angle.

Example - 11

Which of the following species have same shape/same bond order ?

$$N_3^-, NO_2^-, CO_2, O_3$$

Sol. Isoelectronic species have same shape/same bond order. The number of outer electrons is same in CO_2 and N_3^- and same in O_3 and NO_2^-.

Example - 12

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

Sol. The H_2O molecule has a dipole moment of 1.84 D. There are two OH bonds in H_2O molecule. The O–H bonds are polar and has dipole moment of 1.5 D. Since the water molecule has a net dipole, hence the two O–H dipoles are not in a straight line opposing each other. This rules out the linear structure (H–O–H) for water. The two O–H bonds cannot lie along the same line in the same direction also. Therefore, the two O–H bonds in H_2O molecule must be inclined to each other at certain angle. Thus, H_2O molecule has an angular shape.

The CO_2 molecule has zero dipole moment. In CO_2, there are two C = O bonds. Each C = O bond is a polar bond. This means each bond has a dipole moment. Since, the net dipole, and hence the two bonds must be just opposite to each other, i.e., the two bonds must be at 180° relative to each other. Thus CO_2 is a linear molecule.

Example - 13

Is there any change in the hybridization of B and N atoms as a result of the following reaction ?

$$BF_3 + NH_3 \longrightarrow \mathbf{F_3B \leftarrow NH_3}$$

Sol. Here, B atom in BF_3 is sp^2 hybridized and one of its p orbital is empty. N in NH_3 is sp^3 hybridized and are of its hybrid orbitals is occupied by a lone-pair of electrons. During the reaction a coordinate bond is formed due to one-side sharing of electron pair.

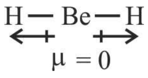
$$BF_3 + NH_3 \longrightarrow [F_3B \leftarrow :NH_3]$$

There is no change in the hybridization of any of the two atoms in this reaction.

Example - 14

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

Sol. This is because BeH_2 is a linear molecule and the two bond dipoles oriented at an angle of 180° neutralize each other. As a result, the net dipole moment of the molecule is zero.



Example - 15

Describe the change in hybridization (if any) of the Al atom in the following reaction.

$$AlCl_3 + Cl^- \rightarrow AlCl_4^-$$

Sol. $$AlCl_3 + Cl^- \rightarrow \underset{\substack{\text{tetrahedral geometry} \\ sp^3 \text{ hybridization}}}{AlCl_4^-}$$

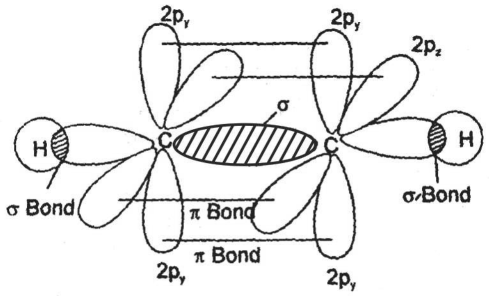
Aluminium chloride exists as dimer Al_2Cl_6. In this molecule chlorine atoms are arranged tetrahedrally around the two Al atoms.

Thus Al atoms show Sp^3 hybridisation in Al_2Cl_6. Thus, there is no change in the hybridisation of Al atom in the given reaction.

Example - 16

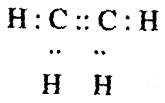
Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in C_2H_4 and C_2H_2 molecules.

Sol. (i) C_2H_4



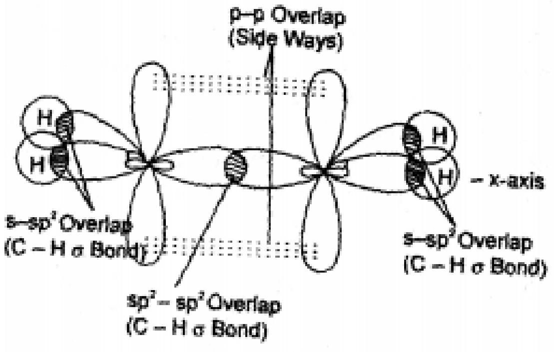
Formation of a double bond between carbon atoms in C_2H_4

The Lewis structure of ethylene is represented as



$$\begin{array}{c} H:\underset{\cdot\cdot}{C}::\underset{\cdot\cdot}{C}:H \\ H \quad H \end{array}$$

(ii) C_2H_2



Formation of C_2H_2 molecule.

It is clear that the carbon-carbon triple bond is made up of one strong $\sigma-$bond and two weak $\pi-$bonds. The Lewis structure of acetylene can be represented as

$$H : C :: C : H$$

Example - 17

Does Li_2 exist ? If so, estimate its bond order and compare its bond dissociation energy with that of H_2.

Sol. Li has a configuration : $1s^2, 2s^1$.

There are two s orbitals (1s and 2s) on each atom. These combine to give four MO's. These are

$$(1s) + (1s) \rightarrow \sigma 1s + \sigma^* 1s$$

$$(2s) + (2s) \rightarrow \sigma 2s + \sigma^* 2s.$$

Thus all the six electrons are accommodated in these four orbitals. The electronic configuration for Li_2 is $(\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2$.

$$N_b = 4, N_a = 2.$$

Bond order in $Li_2 = \dfrac{4-2}{2} = 1.$

Therefore, Li_2 should be a stable species. Its bond dissociation energy is 105 kJ mol^{-1}, as compared to 431 kJ mol^{-1} for H_2. Thus, the bond in Li_2 is much weaker than that on H_2. This is because 2s orbital of Li (involved in the bonding) is much larger than 1s orbital of H.

Example - 18

Explain how V.B theory differs from the Lewis concept.

Sol. The Lewis concept of describes the formation of bond in terms of sharing of one or more electron pairs and the octet rule. It does not explain the energetics of the bond formation and shapes of the polyatomic molecules.

The VB theory describes the bond formation in terms of hybridization and overlap of the orbitals. The overlap of orbitals along the intermolecular axis increases the electron-density between the two nuclei resulting in a decrease in the energy and formation of a bond.

Example - 19

Why is it that in the SF_4 molecule, the lone pair of electrons occupies and equatorial position in the overall trigonal bi-pyramidal arrangement in preference to an axial position.

Sol. In SF_4 molecule, the line pair of electrons occupies an equatorial position because in this geometry (sp^3d hybridisation), the line pair-bond pair repulsion is minimum

Example - 20

Define hydrogen bond. Is it weaker or stronger than the Van der Waals forces ?

Sol. The hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule. A hydrogen bond is shown by a dotted line (.....)

Hydrogen bond is than the Van der Waals forces.

Example - 21

$NaNO_3$ on heating to 500°C decomposes to produce $NaNO_2$ and O_2, while the same salt on heating to 800°C, decomposes to Na_2O, N_2 and O_2. Explain in light of Fajan's rule.

Sol. The decomposition scheme can be shown as

$$\begin{tikzcd} NaNO_4 \arrow[r, "500^\circ C"] & NaNO_2 + O_2 \arrow[d, "800^\circ C"] \\ NaNO_3 \arrow[r, "800^\circ C"] & Na_2O + N_2 + O_2 \end{tikzcd}$$

As we know tha thermal stability of a salt depends on percentage ionic character, $NaNO_2$ has greater ionic character than $NaNO_3$ because of lower polarizability of smaller nitrite ion than nitrate ion. Therefore, 500°C is sufficient for decomposition of less ionic $NaNO_3$ but $NaNO_2$ is stable at this temperature. On heating further to 800°C, the more stable $NaNO_2$ decomposes further to Na_2O and N_2, O_2.

Example - 22

Out of σ and $\pi -$bonds, which one is stronger and why ?

Sol. $\sigma -$bond is stronger. This is because $\sigma -$bond is formed by head-on overlapping of atomic orbitals and, therefore, the overlapping is large. $\pi -$bond is formed by sideway overlapping which is small.

Example - 23

Out of p-orbital and sp-hybrid orbital which has greater directional character and why ?

Sol. sp-orbital has greater directional character than p-orbital. This is because p-orbital has equal sized lobes with equal electron density in both the lobes wheres sp-hybrid orbital has greater electron density on one side.

Example - 24

Compare the relative stabilities of O_2^- and N_2^+ and comment on their magnetic (paramagnetic or diamagnetic) behaviour.

Sol. M.O. Electronic configuration of

$$O_2^- = KK\,\sigma_{2s}^2\ \sigma_2^{*2}\ \sigma_{2p_z}^2\,\pi_{2p_x}^2\ \pi_{2p_x}^2\ \pi_{2p_x}^{*2}\ \pi_{2p}^{*1}$$

$$\text{Bond order} = \frac{1}{2}(8-5) = \frac{3}{2} = 1.5$$

M.O. Electronic configuration of

$$N_2^+ = KK\,\sigma_{2s}^2\ \sigma_{2s}^{*2}\ \pi_{2p_x}^2\ \pi_{2p}^2\ \sigma_{2p_z}^1$$

$$\text{Bond order} = \frac{1}{2}(7-2) = \frac{5}{2} = 2.5$$

As bond order of $N_2^+ >$ bond order of O_2^-, therefore, N_2^+ is more stable than O_2^-.

Each of them contains unpaired electron, hence both are paramagnetic.

Example - 25

Explain why HF is less viscous than H_2O.

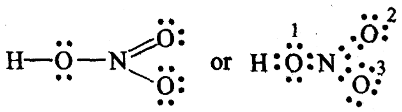
Sol. There is greater intermolecular hydrogen bonding in H_2O than that in HF as each H_2O molecule forms four H-bonds with other water molecules whereas HF forms only two H-bonds with other HF molecules. Greater the intermolecular H-bonding, greater is the viscosity. Hence, HF is less viscous than H_2O.

Example - 26

Write Lewis structure of the following compounds and show formal charge on each atom :

HNO_3, NO_2, H_2SO_4

Sol. $HNO_3 =$



$$\text{Formal charge} = V - L - \frac{1}{2}S$$

$$\text{Formal charge on H} = 1 - 0 - \frac{1}{2} \times 2 = 0$$

$$\text{Formal charge on O (1)} = 6 - 4 - \frac{1}{2}(4) = 0$$

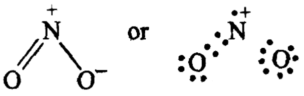
$$\text{Formal charge on N} = 5 - 0 - \frac{1}{2}(8) = 1$$

$$\text{Formal charge on O (2)} = 6 - 4 - \frac{1}{2}(4) = 0$$

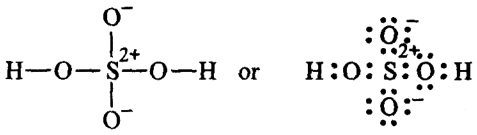
$$\text{Formal charge on O (3)} = 6 - 6 - \frac{1}{2}(2) = -1$$

Hence, we write the structure of HNO_3 with formal charges as

Similarly, we have



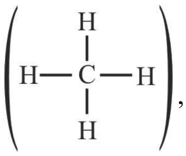
and



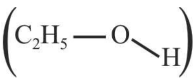
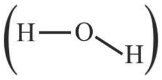
Example - 27

What is mean by the term average bond ethalpy ? Why is there difference in bond enthalpy of O–H bond in ethanol (C_2H_5OH) and water ?

Sol. All the similar bonds in a molecule do not have the same bond enthalpies, e.g., in CH_4, the four



C–H bonds do not have the same bond enthalpies because after breaking of the bonds one by one, the electronic environment around carbon changes. Hence, the actual bond enthalpy of C–H bond is taken as the average value.

O–H bond in ethanol  and that in water  do not have similar electronic environment around oxygen atom. Hence, their O–H bond enthalpies are different.

Example - 28

Write Lewis dot structures of the following molecules/ ions :

(i) CO (ii) HCN

Sol : V = number of valence electron of molecule

R = Number of electron required for octet in molecule

S = Number of shared electron (S = R – V)

U = Number of unshared electron (U = V – S)

(i) CO

V = 4 + 6 = 10 electrons

R = 8 + 8 = 16 electrons

S = R – V = 6 electrons

U = 10 – 6 = 4 elctrons

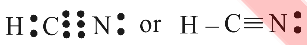
(ii) HCN

V = 1 + 4 + 5 = 10 electrons

R = 2 + 8 + 8 = 18 electrons

S = 8 electrons

U = 2 electrons



Example - 29

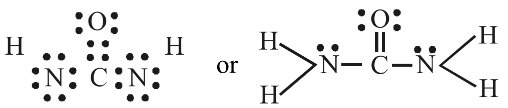
Write Lewis structures for

(i) Urea, $NH_2CO\,NH$

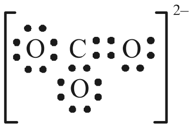
(ii) Carbonate ion, CO_3^{2-}.

Sol : (i) Urea, V = 24 electrons, R = 40 electrons, S = 16 electrons

U = 8 electrons



(ii) V = 24 electrons, R = 32 electrons, S = 8 electrons, U = 16 electrons.



Example - 30

Arrange the following in increasing order of bond angle around the central atom :

BeF_2, BF_3, CH_4, NH_3, H_2O

Sol. $H_2O < NH_3 < CH_4 < BF_3 < BeF_2$

Bond angle 104.5° 106.5° 109°28’ 120° 180°

Example - 31

Indicate the number of σ and π-bonds in the following molecules.

(i) $CH_3-CH=CH_2$

(ii) $CH_3-CH_2-CH_2-CH_3$

(iii) $CH_3-C\equiv C-CH_3$

(iv) 

Sol. For finding out the number of σ and π-bonds in a molecule, the following points should be kept in mind :

1. All single bonds are sigma bonds.
2. All double bonds consist of one σ and two π-bonds.
3. All triple bonds consist of one σ and two π-bonds.

(i) This molecule consists of seven single bonds and one double bond. Thus, number of σ-bonds = 8 and number of π-bonds = 1.

(ii) This molecule consists of 13 single bonds.

Thus, number of σ-bonds = 13.

(iii) This molecule consists of 8 single bonds and one triple bond. Thus, number of σ-bonds = 9 and number of π-bonds = 2.

(iv) The molecule of benzene consists of nine single bonds and three double bonds.

Thus, number of σ-bonds = 12 and number of π-bonds = 3.

Example - 32

Which of the two, peroxide ion or superoxide ion, has a larger bond length ?

Sol. The bond length in a molecule depends on bond order. the higher the bond order, smaller will be the bond length.

Peroxide ion, O_2^{2-}

Configuration KK $\sigma(2s)^2 \overset{*}{\sigma}(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2$

$$\pi(2p_y)^2 \overset{*}{\pi}(2p_x)^2 \overset{*}{\pi}(2p_y)^2$$

$$\text{Bond order} = \frac{8-6}{2} = 1$$

Superoxide ion, O_2^{-}

Configuration KK $\sigma(2s)^2 \overset{*}{\sigma}(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2$

$$\pi(2p_y)^2 \overset{*}{\pi}(2p_x)^2 \overset{*}{\pi}(2p_y)^1$$

$$\text{Bond order} = \frac{8-5}{2} = 1.5$$

Bond order of superoxide is higher than peroxide ion, hence bond length of peroxide ion is larger.

Example - 33

Which of the following has maximum bond angle ?

H_2O, CO_2, NH_3, CH_4

Sol. CO_2 (Linear structure, carbon undergoes sp-hybridization).

Example - 34

Interpret the non-linear shape of H_2S molecule and non planar shape of PCl_3 using valence shell electron pair repulsion (VSEPR) theory.

Sol. In H_2S, two bonded pairs and two lone pairs of electrons are present, i.e., S undergoes sp^3 -hybridization. Tetrahedral configuration comes into existence. Two of the positions are occupied by lone pairs, hence the actual structure is bent or V-shaped.

In PCl_3, three bonded pairs and one lone pair of electrons are present, i.e., P-atom undergoes sp^3– hybridization. Tetrahedral configuration comes into existence. One position is occupied by lone pair, hence the actual structure is pyramidal.

Example - 35

Hydrogen bonding does not exist in HCl through chlorine is quite electronegative.

Sol. This is due to the large size of Cl-atom

Example - 36

The dipole moment of KCl is 3.336×10^{-29} coulomb metre which indicates that it is a highly polarized molecule. The interatomic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10} m. Calculate the dipole moment of KCl molecule, if there were opposite charges of one fundamental unit located at each nucleus. Calculate the percentage ionic character of KCl.

$\mu = q \times d$

Sol. q = one fundamental unit $= 1.062 \times 10^{-19}$ C

$d = 2.6 \times 10^{-10}$ M

$= 1.602 \times 10^{-19} \times 2.6 \times 10^{-10}$

$= 4.1652 \times 10^{-29}$ coulomb metre

Percentage ionic character

$$= \frac{3.336 \times 10^{-29}}{4.1652 \times 10^{-29}} \times 100 = 80.09$$

Example - 37

The correct order of the ionic character of PbF_2, $PbCl_2$, $PbBr_2$ and PbI_2 is :

(a) $PbF_2 > PbCl_2 > PbBr_2 > PbI_2$

(b) $PbF_2 > PbBr_2 > PbCl_2 > PbI_2$

(c) $PbF_2 < PbCl_2 < PbBr_2 < PbI_2$

(d) $PbF_2 < PbCl_2 > PbBr_2 > PbI_2$

Sol. Since the given dihalides contain the same cation viz Pb^{2+} but different anions (halide ions), the ionic character of these halides depends on the size of the halide ions. The ionic character decreases with the increases in the size of the halide ions. Thus since the size of halides ions increases as $F^- < Cl^- < Br < I^-$, the ionic character of $Pb\,X_2$ molecules decreases as $PbF_2 > PbCl_2 > PbBr_2 > Pb\,I_2$. Thus (a) is the correct answer.

Example - 38

Among the halides namely, NaF, NaCl, NaBr and NaI, NaF has the highest melting point, because NaF has :

(a) minimum ionic character

(b) maximum ionic character

(c) highest oxidising power

(d) lowest valency

Sol. Since the size of halide ions (X^-) increases as $F^- < Cl^- < Br^- < I^-$ the ionic character of MX molecules decreases as NaF > NaBr > NaI. Being the most ionic, NaF has the highest melting point.

Example - 39

A diatomic molecule has a dipole moment equal to 1.2 D. If its bond distance is 1.0 Å, what fraction of an electronic charge exists in each atom ?

(a) 12% **(b) 18%**

(c) 25% **(d) 29%**

Sol. Bond distance, d = 1.0 Å = 1.0×10^{-8} cm (given)

Dipole moment, $\mu = 1.2\ D = 1.2 \times 10^{-18}$ esu. cm (given)

Electronic charge = 4.8×10^{-18} esu. cm (given)

Fraction of electronic charge = x (to be calculated)

Now we know that :

$$\mu = x \times d$$

$$1.2 \times 10^{-18}\ \text{esu. cm} = x \times 10^{-8}\ \text{cm}$$

$$\therefore\ x = \frac{1.2\times10^{-18}\ \text{esu. cm}}{10^{-8}\ \text{cm}} = 1.2\times10^{-10}\ \text{esu}$$

Out of 4.8×10^{-10} esu. cm electronic charge, the electronic charge existing on each atom = 1.2×10^{-10} esu

$\therefore$ Out of 100 esu. cm. electronic charge, the electronic charge existing on each atom

$$= \frac{1.2\times10^{-10}\ \text{esu}}{4.8\times10^{-10}\ \text{esu. cm}}\times100$$

$$= 25\%$$

Example - 40

Which of the following tetraiodides is the least stable and has doubtful existence ?

(a) CI_4 **(b) GeI_4**

(c) SnI_4 **(d) PbI_4**

Sol. The given tetraiodides contain C, Ge, Sn and Pb as C^{4+}, Sn^{4+} and Pb^{4+} ions respectively. According to inert pair effect, the stability of these cations decreases as $C^{4+} > Ge^{4+} > Sn^{4+} > Pb^{4+}$. This order shows that since Pb^{4+} ion is the least stable, its tetraiodide, PbI_4 is also least stable and hence has doubtful existence.

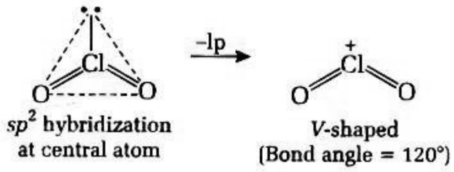
Example - 41

Discuss the bondings of ClO_2^+ ion.

Sol. The central atom is $Cl^\bullet$. The ions can be constituted as

EP at central atom = 2(σ) + 1(lp) = 3

Geometry :

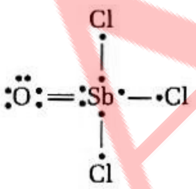


Example - 42

Write the Lewis dot formula of the following molecules and predict their molecular shapes :

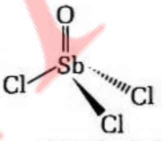
(a) $OSbCl_3$ (b) SO_2Cl_2 (c) $IO_2F_2^-$

Sol. (a)



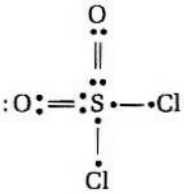
EP at Sb = 4, sp^3

Shape =



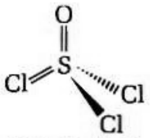
(Tetrahedral)

(b) SO_2Cl_2



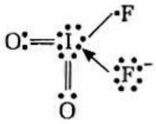
EP at S = 4, sp^3

Shape =



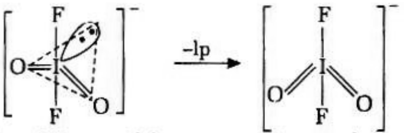
(Tetrahedral)

(c) $IO_2F_2^-$:



EP = 5, sp^3d hybridized I.

Shape :



Trigonal bipyramidal geometry

See-saw shape

Example - 43

In vapour phase, phosphorus can exist as P_2 molecules, which is highly reactive, whereas N_2 is relatively inert, exaplain the difference.

Sol. Both P and N are from the same group (G15) of the Periodic Table, their diatomic molecule can be represented as :

$$\ddot{P}\equiv\ddot{P} \quad \text{and} \quad \ddot{N}\equiv\ddot{N}$$

As we know, Pi-bonding between two phosphorus atoms is very unlikely due to larger atomic radius. Hence, diatomic P_2 is unstable but there is not such restriction of Pi-bonding to N and other second period elements.

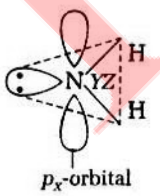
Example - 44

Both NH_2^- and NH_2^+ are angular species but the bond angle in NH_2^- is less than that in NH_2^+. (a) What is the reason for this difference in bond angles ? (b) Take the x-axis as lying perpendicular to the molecular plane, does N ($2p_x$) orbital participate in the hybridization of either of species ?

Sol. (a) Hybridization at N atom is sp^3 in NH_2^- and sp^2 NH_2^+.

Therefore, bond angle in NH_2^- is close to 109° (tetrahedral angle), while bond angle in NH_2^+ is close to 120° (triangular planar angle).

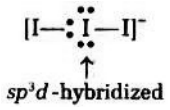
(b) In NH_2^-, hybridization at N is sp^3 $\Rightarrow$ implies that all p-orbitals are involved in hybridization. In case of NH_2^+, the hybridization at N is sp^2 and the ion lies in YZ plane as X-axis lying in perpendicular plane. For the species to be in YZ plane, the two p-orbitals involved in sp^2 hybridization must be p_y and p_z orbitals i.e., $2p_x$ orbitals at N is remaining unhybridized as



Example - 45

Although I_3^- is known, F_3^- is not. Explain.

Sol. In I_3^-, the central I is sp^3d hybridized and violate the octet rule. It is possible for elements of third and higher period to expand its valence shell beyond eight because they contain vacant d-orbitals. Hence formation of I_3^- is possible



Since, fluorine is in second period, lack vacant d-orbitals, can't violate octet rule and, hence F_3^- does not exist.

Example - 46

Iodine (I_2) is a volatile solid at room temperature and has very low solubility in water. However, I_2 is highly soluble in an aqueous solution of KI. Explain.

Sol. I_2 (s) being a molecular solids, the molecules are completely non-polar and covalent, have very low affinity for polar solvents like water. However, in solution of KI, I_2 forms forms KI_3 salt as

$$KI + I_2 \longrightarrow KI_3$$

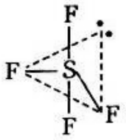
KI_3, a strongly ionic salt dissolves easily in water like other normal salts of the alkali metals. Hence, I_2 becomes soluble in KI via KI_3.

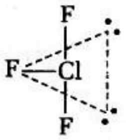
Example - 47

Compare the F (axial) —A—F (equatorial) bond angles in these molecules. PF_6, SF_4 and ClF_3.

Sol. PF_5 is symmetrical trigonal bipyramidal molecule hence the sought bond angle is 90°.

SF_4 is a see-saw shaped molecule, while ClF_3 is T-shaped as shown below :

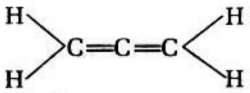




Axial bonds in SF_4 is repelled by one lone pair, the same in ClF_3 are repelled by two lone pairs, more repulsions are observed in ClF_3. Hence, F—S—F angle (axial-equatorial) is greater than F—Cl—F (axial-equatorial), although both are less than 90°. The order is : $PF_5 > SF_4 > ClF_3$.

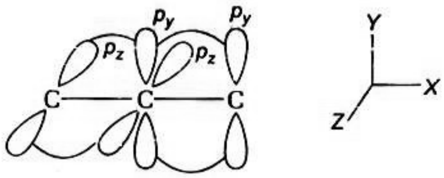
Example - 48

The Lewis structure of allene is

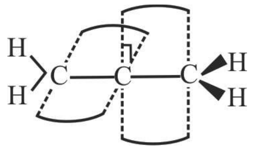


Make a three dimensional sketch of this molecule and answer these questions : (a) Is the molecule planar ? (b) Does 1,3-dichloro propdience show geometrical isomerism ? (c) Is the molecule 1,3-dichloropropdiene polar ?

Sol. Hybridization of central carbon is sp and two of its unhybridized p-orbitals are involved in Pi-bonding. Also p-orbitals at an atom are orthogonal (at 90° angle), the two Pi-bonds at central carbon are also orthogonal. Let these p-orbitals, involved in Pi-bondings, at central carbon by p_y and p_z, then



Hybridization at the terminal carbons are both sp^2. The two p-orbitals involved in sp^2 hybridization are p_x and p_y at left terminal and p_x and p_z at right terminals. Therefore, the three sp^2 hybrid orbitals at left terminal carbon are in xy plane, while the same at right terminal carbon are in xz plane. As a result, the two triangular planes at terminals are at right angles as shown below :



The two H—C—H planes at terminals are perpendicular to each other. (Pi-bonds are also perpendicular to each other.)

Hence, (a) Molecule is non-planar. (b) Doesn't show geometrical isomerism because two H at one terminal are equidistant from any H on other terminal. (c) Polar.

Example - 49

Order these species according to increasing C—F bond length : CF^+, CF, CF^-. Predict if any is paramagnetic.

Sol. The molecular orbital electronic configuration of CF (15e) is

$$\sigma 1s^2 \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_x^2 \left|\begin{matrix}\pi 2p_y^2 \\ \pi 2p_z^2\end{matrix}\right| \left|\begin{matrix}\pi^* 2p_y^1 \\ \pi^*\ 2p_z^0\end{matrix}\right| \sigma^* 2p_x^0$$

$$\text{Bond order} = \frac{10-5}{2} = 2.5$$

In CF^+, there is one 'e' less in antibonding MO, therefore, bond-order = 3, while in CF^-, there is one more 'e' in antibonding MO giving band-order = 2. Since 'Bond-order' is directly related to bond-energy, which is inversely proportional to bond-length, the order of bond-lengths in given series is :

$$CF^+ < CF < CF^-$$

Also, CF and CF^- are paramagnetic because of presence of one and two unpaired electrons respectively, while CF^+ has no unpaired electron and diamagnetic.

Example - 50

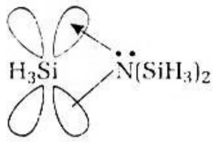
Both 'H' and 'F' are monovalent in covalent bonding, phosphorus forms PF_5 but no PH_5 exists. Explain.

Sol. Phosphorus has five electrons in the valence shell ($3s^2 3p^3$) as well as it contains vacant 3d 3d orbitals, so there is scope for pentavalency. However, the 3d orbital of phosphorus is much larger is size than its 3s and 3p-orbitals, and do not usually hybridize. When highly electronegative atoms like F approach to P, its 3d-orbitals, and do not usually hybridize. When highly electronegative atoms like F approach to P, its 3d-orbitals hybridize with 3s and 3p orbitals and enable P to undergo sp^3d hybridization to form PF_5, PCl_5 etc. Hydrogen being very less electronegative, cannot contract 3d orbitals of phosphorus to the level where it can participate in hybridization with 3s and 3p orbitals. Hence, with hydrogen, only s and p orbitals of P hybridize and no more than its three electrons can take part in sharing, showing trivalency only.

Example - 51

Trimethyl amine is a stronger base than trisilyl amine. Explain.

Sol. In trisilyl amine, a pπ-dπ back bonding occurs as



The above pπ-dπ bond decreases the availability of 1p at nitrogen, thus the basic strength. No such pπ-dπ bonding is possible in trimethyl amine, hence stronger base.

STATE OF MATTER

INTRODUCTION

Any substance that has mass and occupies space is called Matter. Matter is composed of atoms or molecules. The arrangement of these building blocks gives matter various states, physical and chemical properties. The force of interaction between these particles give matter its physical properties based on which matter can be classified into solid, liquid or gases. The force of interaction between atoms/ molecules is **highest in solids** and **least in liquids.**

In this unit, we will learn more about these three physical states of matter particularly liquid and gaseous states.

1. INTERMOLECULAR FORCES

The forces of attraction existing among the molecules of a substance (gaseous, liquid or solid) are called intermolecular forces.

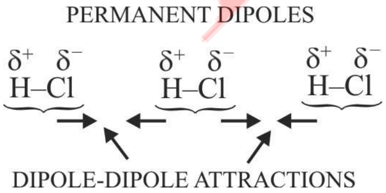
Dipole-dipole, dipole-induced dipole and dispersion forces are collectively called as van der Waals forces. Ion-dipole and ion-induced dipole forces are not van der Waals forces. Further, hydrogen bonding is only a special type of dipole-dipole attraction shown only by limited number of elements.

The different types of intermolecular forces are :

1.1 Dipole-Dipole Interactions

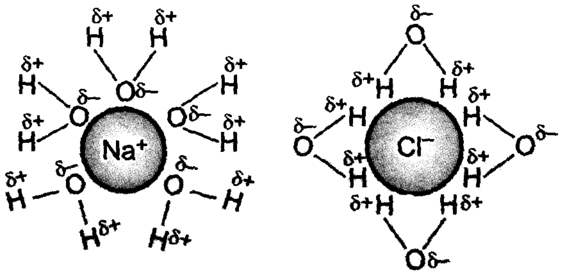
These forces of attraction occur among the polar molecules. Polar molecules have parmanent dipoles. The positive ple of one molecule is thus attracted by the negative pole of the other molecule.

HCl in which chlorine being more electronegative acquires a slight negative charge whereas the hydrogen end becomes slightly positively charged. The dipole-dipole interactions then take place among the HCl molecules :



1.2 Ion-Dipole Interactions

This is the attraction between an ion (cation or anion) and a polar molecule. For example, when NaCl is dissolved in water, the polar water molecules are attracted towards Na^+ ion as well as towards Cl^- ion.



Ion-dipole attractions between Na^+ and H_2O molecules and Cl– ion and H_2O molecules

1.3 Ion-Induced dipole Interactions

A non-polar molecule may be polarized by the presence of an ion near it, i.e., it becomes an induced dipole. The interactions between them are called ion-induced dipole interactions.

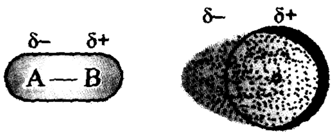
Ion-induced dipole attractions

between NO_3^- ion and I_2 molecule

For example, in the presence of nitrate ion (NO_3^-), iodine molecule (I_2), which is non-polar, gets polarized as $(\overset{\delta+}{I} - \overset{\delta-}{I})$ as shown in fig.

1.4 Dipole-Induced dipole Interactions

A non-polar molecule may be polarized by the presence of a polar molecule (dipole) near it, thereby making it an induced dipole. The interactions between them are then called dipole-induced dipole interactions.

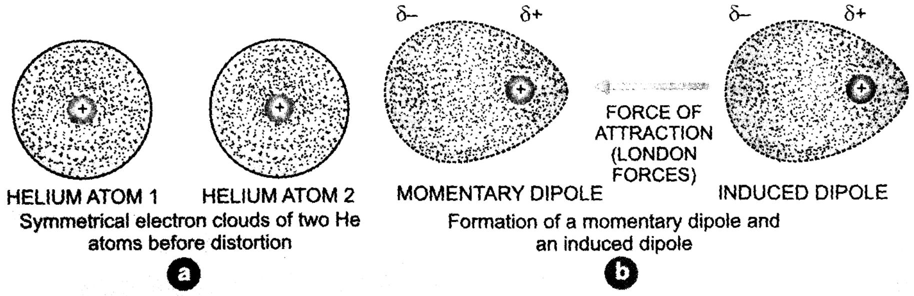


Dipole-induced dipole attractions

For example, noble gases get polarized in the presence of polar molecules.

1.5 London forces or Dispersion forces

At any instant of time, the electron cloud of the molecule may be distorted so that an instantaneous dipole or momentary dipole (i.e., a dipole for a short while) is produced in which one part of the molecule is slightly more negative than the rest. The momentary dipoles induce dipoles in the neighbouring molecules. These are then attracted to each other. The forces of attraction between the induced momentary dipoles are called London dispersion forces.



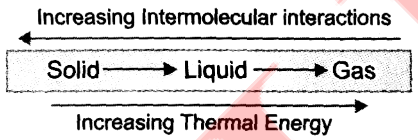
Forces of attraction between momentary dipoles and induced dipoles (London forces) in helium atoms

2. INTERMOLECULAR FORCES VERSUS THERMAL ENERGY

Whether a substance will exist as a solid or a liquid or a gas is the result of competition between :

(i) intermolecular forces, i.e., the forces of interaction between the molecules of that substance which try to bring the molecules closer, and

(ii) thermal energy possessed by the molecules due to temperature which results into the movement of the molecules and hence tries to keep them apart.



3. IDEAL GAS

An ideal gas is a **hypothetical concept** of matter and is treated as a standard of comparison while studying the various states of matter. There are various assumptions associated with an ideal gas. The most notable of these assumptions are:

- Volume of the molecules are infinitely small and the force of interaction between the molecules is zero
- The molecules of the gas undergo random motion colliding with each other and the walls of the container
- Laws of classical mechanics are applicable on the molecules.

4. STATE OF A GAS AND STATE VARIABLES

"State" of a gas means the physical condition of the system. Certain variables are used to represent physical condition of the gas which are termed as **state variables.**

There are majorly three variables for a given sample of a gas, i.e. **Pressure, Volume and Temperature (P, V and T).** When the values of these three parameters are fixed for a gas, we say it to be in a fixed state.

4.1 Pressure

A force is exerted on the walls of the container due to the collisions of the atoms/molecules. This force averaged per unit area is called the pressure.

4.1.1 Measurement of pressure of a gas

The most common instrument used to measure the pressure of a gas is called a **barometer.** Another instrument used to measure pressure is **manometer.**

4.2 Volume

In case of rigid containers, the volume of the gas is same as the volume of the container it is kept in. However, for containers which can expand (e.g. balloon), the volume of the gas is determined by the other two state functions and **moles of the gas taken.**

4.3 Temperature

Temperature is a measure of the amount of heat contained in the gas. When the temperature of the gas equals the surrounding temperature, no heat flows in or out of the gas and the gas is said to be in a state of **Thermal Equilibrium.**

4.3.1 Measurement of Temperature

The instrument used to measure the temperature of a gas is called a thermometer. There are three units used in measuring temperature viz. °C, °F and K.

Pressure relations	Temperature relations	Volume relations
1 atm = 1.0132×10^5 Pa	1.8 T (^{0}C) = T (^{0}F) – 32	1 L = 1000 mL
1 bar = 10^5 Pa	T (K) = T (^{0}C) + 273.15	1 m^3 = 1000 L
76 cm Hg = 1 atm = 760 mm Hg		1 mL = 1 cc
1 torr = 1 mm Hg		1 dm^3 = 1 L
1 kPa = 1000 Pa		

5. IDEAL GAS LAW

There are four laws which relate the state variables of a gas in two states. These four laws are :

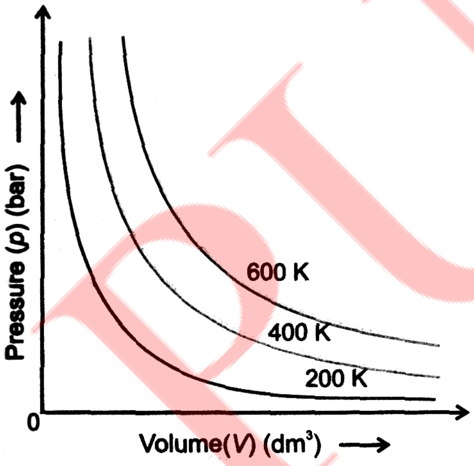
5.1 Boyle's Law (Pressure – Volume Relationship)

It states that at constant temperature, the pressure of a fixed amount (i.e. number of moles n) of gas varies inversely with its volume. This is known as Boyle's law Mathematically

$$p \propto \frac{1}{V} \text{ (at constant T and n)}$$

PV = constant

$$\Rightarrow p_1V_1 = p_2V_2$$

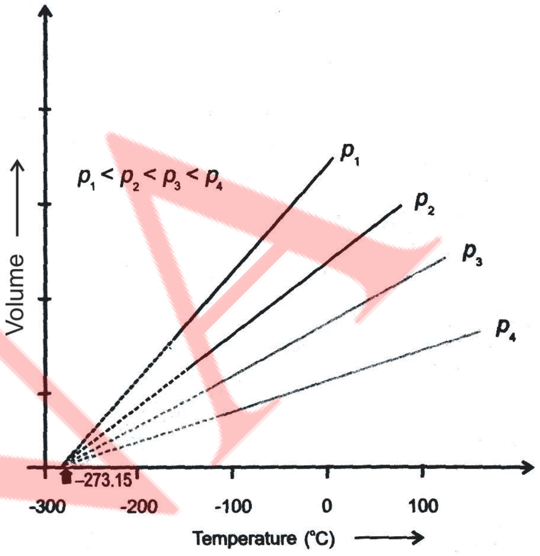


Graph of pressure, p vs. Volume, V of a gas at different temperature

Each curve corresponds to a different constant temperature and is known as an isotherm.

5.2 Charles's Law (Temperature - Volume Relationship)

It states the pressure remaining constant, the volume of a fixed mass of a gas is directly proportional to its absolute temperature.



Each line of the volume vs temperature graph is called isobar.

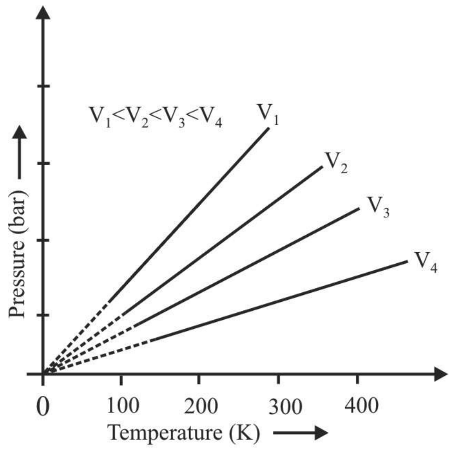
5.3 Gay Lussac's Law (Pressure-Temperature Relationship)

It states that at constant volume, pressure of a fixed amount of a gas varies directly with the temperature. Mathematically,

$$p \propto T$$

$$\Rightarrow \frac{P}{T} = \text{constant}$$

Each line of pressure is temperature graph is called isochore.



Pressure vs temperature (K) graph (Isochores) of gas.

5.4 Avogadro Law (Volume - Amount Relationship)

It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules.

Mathematically

$V \propto n$ where n is the number of moles of the gas.

6. IDEAL GAS EQUATION

The above laws can be combined together in a single equation which is known as ideal gas equation.

At constant T and n; $V \propto \frac{}{p}$ Boyle's Law

At constant p and n; $V \propto T$ Charles's Law

At constant p and T; $V \propto n$ Avogadro Law

Thus,

$$V \propto \frac{nT}{p}$$

$$\Rightarrow \quad V = R\frac{nT}{p}$$

where R is proportionality constant. On rearranging the equation we obtain

$pV = nRT$

This equation is called ideal gas equation.

$$\Rightarrow \quad R = \frac{pV}{nT}$$

R is called gas constant. It is same for all gases. Therefore it is also called universal gas constant.

Values of R :

(i) $R = 8.314\ J\ K^{-1}\ mol^{-1}$, (ii) $R = 0.0821\ L\ atm\ K^{-1}\ mol^{-1}$.

(iii) $R = 2\ cal\ K^{-1}\ mol^{-1}$.

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

$$\frac{p_1V_1}{T_1} = nR \quad \text{and} \quad \frac{p_2V_2}{T_2} = nR$$

$$\Rightarrow \quad \frac{p_1V_1}{T} = \frac{p_2V_2}{T_2}$$

This equation is alos known as combined gas law.

7. VARIATION OF THE IDEAL GAS EQUATION

Ideal gas equation can be rearranged as follows :

$$\frac{n}{V} = \frac{p}{RT}$$

Replacing n by $\frac{m}{M}$, we get

$$\frac{m}{MV} = \frac{p}{RT}$$

$$\frac{d}{M} = \frac{p}{RT} \text{ (where d is the density)}$$

$\Rightarrow pM = dRT$

8. DALTON'S LAW OF PARTIAL PRESSURES

It states that the total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases i.e., the pressures which these gases would exert if they were enclosed separately in the same volume and under the same conditions of temperature. In a mixture of gases, the pressure exerted by the individual gas is called partial pressure. Mathematically,

$p_{Total} = p_1 + p_2 + p_3 + ...$ (at constant T, V)

where p_{Total} is the total pressure exerted by the mixture of gases and p_1, p_2, p_3 etc. are partial pressures of gases.

Partial pressure in terms of mole fraction

Suppose at the temperature T, three gases, enclosed in the volume V, exert partial pressure p_1, p_2 and p_3 respectively. then,

$$p = \frac{n_1RT}{V}$$

$$p_2 = \frac{n_2RT}{V}$$

$$p_3 = \frac{n_3RT}{V}$$

where n_1 n_2 and n_3 are number of moles of these gases. Thus expression for total pressure will be

$p_{Total} = p_1 + p_2 + p_3$

$$= n\frac{RT}{V} + n_2\frac{RT}{V} + n_3\frac{RT}{V}$$

$$= (n_1 + n_2 + n_3)\frac{RT}{V}$$

On dividing p_1 by p_{total} we get

$$\frac{p_1}{p_{total}} = \left(\frac{n_1}{n_1 + n_2 + n_3}\right)\frac{RTV}{RTV}$$

$$= \frac{n_1}{n_1 + n_2 + n_3} = \frac{n_1}{n} = x_1$$

where $n = n_1 + n_2 + n_3$

x_1 is called mole fraction of first gas.

Thus, $p_1 = x_1\, p_{total}$

Similarly for other two gases we can write

$p_2 = x_2\, p_{total}$ and $p_3 = x_3\, p_{total}$

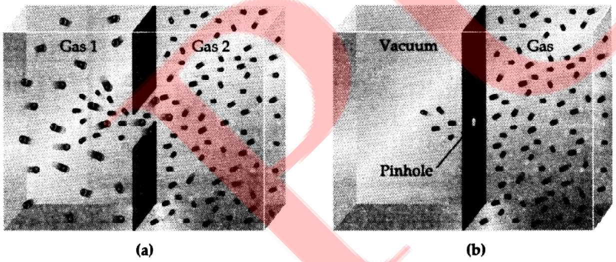
Thus a general equation can be written as

$p_i = x_i\, p_{total}$

9. GRAHAM'S LAW OF DIFFUSION

Diffusion is a process of intermixing of gases. This is a natural tendency of any gas to occupy the whole volume available to it. So even without pressure difference gases mix with each other. If the pressure difference is increased the diffusion process becomes faster.

Effusion is flow of a gas through small openings due to pressure difference that is it is a case of fast diffusion.



(a)

(b)

(a) Diffusion is mixing of gas molecules by random motion under conditions where molecular collisions occur.

(b) Effusion is the escape of a gas through a pinhole without molecular collisions.

According to Graham's Law the rate of diffusion depends on pressure and molecular weight of a gas. Rate of Diffusion is directly proportional to Partial Pressure of the gas and inversely proportional to the square root of molar mass of the gas. That is, greater the pressure faster is the movement of molecules and heavier the molecules, slower are their movement.

Rate of diffusion $\propto$ P (partial pressure)

Also, $\propto 1/\sqrt{M}$

Therefore we can write:

Rate, r $\propto P/\sqrt{M}$

Rate of diffusion may be defined in various ways. It may be number of moles transferred per unit time, Volume transferred per unit time, distance travelled per unit time and even pressure drop per unit time. While comparing the rates of two gases, we should take similar definitions of rate, it may be n/t, V/t or d/t.

$$\frac{r_2}{r_1} = \frac{P_2}{P_1}\sqrt{\frac{M_1}{M_2}}$$

Graham's Law can be applied to diffusion and effusion both.

10. KINETIC THEORY OF GASES

Assumptions or postulates of the kinetic-molecular theory of gases are given below. These postulates are related to atoms and molecules which cannot be seen, hence it is said to provide a microscopic model of gases.

(i) Gases consist of large number of identical particles (atoms or molecules) that are so small and so far apart on the average that the actual volume of the molecules is negligible in comparison to the empty space between them.

(ii) There is no force of attraction between the particles of a gas at ordinary temperature and pressure.

(iii) Particles of a gas are always in constant and random motion.

(iv) Particles of a gas move in all possible directions in straight lines. During their random motion, they collide with each other and with the walls of the container. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container.

(v) Collisons of gas molecules are perfectly elastic. This means that total energy of molecules before and after the collision remains same.

(vi) At any particular time, different particles in the gas have different speeds and hence different kinetic energies.

It is possible to show that though the individual speeds are changing, the distribution of speeds remains constant at a particular temperature.

If a molecule has variable speed, then it must have a variable kinetic energy. Under these circumstances, we can talk only about average kinetic energy. In kinetic theory it is assumed that average kinetic energy of the gas molecules is directly proportional to the absolute temperature.

The important mathematical results from this Theory are ;

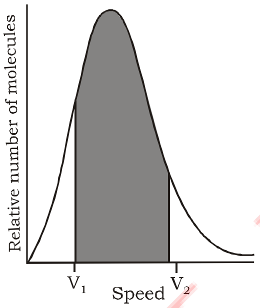
K.E. per mole = 3/2 nRT

K.E. per molecule = 3/2 kT

where R = 8.314 and $k = R/N_A = 1.38 \times 10^{-23}$ J/K

11. Molecular Distribution of speeds (Max well Boltzmann Distribution)

The Maxwell Boltzmann Distribution is a plot of **fraction of molecules in the gas sample** vs. the **speed of the gas molecules.** The distribution is shown below followed by the salient features of the graph.



The graph shows that :

- The fraction of molecules having very low or very high speeds is very less.
- Most of the molecules have a speed somewhere in the middle, this is called the most probable speed. (μ_{MP})
- The area covered between any two velocities is the number of molecules in that velocity range.
- The total area covered by the graph gives the total number of molecules in the sample and is constant.
- There are two more molecular speeds defined for a sample called average speed (u_{AVG}) and root mean square speed (u_{RMS})

$$u_{RMS} = \sqrt{\frac{3RT}{M}} \qquad u_{MP} = \sqrt{\frac{2RT}{M}} \qquad u_{AVG} = \sqrt{\frac{8RT}{\pi M}}$$

NB : ***Always remember to take molecular mass in kg in the above relations.***

It's useful to remember the ratio of $u_{MP} : u_{AVG} : u_{RMS}$ 1:1.128:1.224 for a given gas at the same temperature.

12. REAL GASES

In case of real gases two of assumption taken for ideal gases become invalid or restricted only to some particular conditions.

(i) We assumed that there are no interactions between molecules of an ideal gas.

(ii) We assumed that volume of the molecules of a gas is negligible as compare to entire volume of gases.

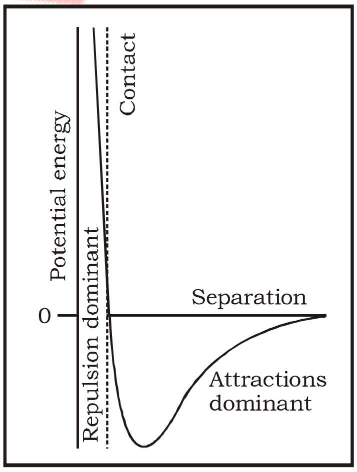
In case of real gases, we cannot ignore the molecular interactions any more.

There are two types of forces of interaction :

Long Ranged attractive forces. &

Short Ranged repulsive forces.

When the molecules of a real gas are far apart, the interactive forces are negligible. When the molecules are brought closer to each other attractive forces start to develop and when the molecules are too close they start repelling each other. The following curve represents the variation of potential energy of a system of two molecules of a real gas with distance between them.



13. COMPRESSIBILITY FACTOR

The deviation from ideal behaviour can be measured in terms of compressibility factor (Z).

$Z = V_m(\text{real})/V_m(\text{ideal})$

- At very low pressures, there are no interactions between the molecules of the real gas and Z = 1.
- At low or moderate pressure, there are attractive forces dominant due to which a real gas is compressed to a greater volume than expected, therefore Z < 1.
- At high pressures, repulsions dominate and it is tough to compress the real gas so it is compressed to smaller volume

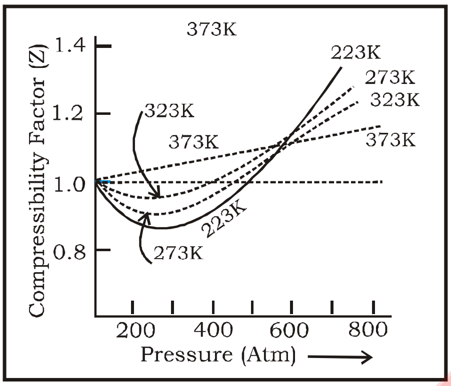
than expected thus Z > 1.

Z is always 1 for ideal gases.

For real gases Z = PV/nRT.

13.1 Variation of Z with P and T

The graph of compressibility factor, Z, with pressure for an ideal gas is a straight line. However, for real gases the value of Z is <1 for low pressures and then Z becomes >1 as pressure increases and keeps on increasing. On increasing the temperature the graph tends more towards Z=1 i.e. ideal gas.



It can be concluded from the above graphs that real gas follows ideal behavior at low pressure and high temperature. This does not mean that if you keep on increasing the temperature a real gas will convert to ideal gas. There is a characteristic temperature at which a gas follows ideal behavior most closely; this is called **Boyle's temperature.**

14. VANDERWALL'S EQUATION

This equation was formulated taking into account correction factors for pressure and volume into the ideal gas equation.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

Constants a and b are called vander waals constants and their value depends on the characteristic of a gas.

Note :

(i) Unit of a $\equiv \frac{L^2\ \text{atm}}{\text{mol}^2}$; b $\equiv \frac{L}{\text{mol}}$

(ii) a ≡ Relates to the forces interacting between the gas molecules and modifies the pressure term.

('a' is high if the gas molecules have more attractive forces)

(iii) b ≡ Relates to the volume occupied by the gas molecules and takes into account the fact that the space actually occupied by the molecules themselves is unavailable for the molecules to move in and is given by :

b = 4 × volume of 1 mol of gas molecules.

(iv) For a given gas Van der Waal's constant 'a' is always greater than 'b'.

(v) The gas having higher values of 'a' can be liquefied easily.

14.1 Applicability of Vanderwaal's Equation

Under the conditions of high temperature and low/moderate pressure and also under very low pressure Z = 1 and the above equation becomes $PV_m = RT$.

14.2 At low/moderate Pressure

The volume correction factor can be ignored and Z<1 where the attractive forces dominate. The equation becomes:

$$Z = \left(1 - \frac{a}{V_m RT}\right)$$

14.3 At high Pressure

The volume correction factor cannot be ignored but the pressure correction factor can be ignored. Z > 1 and the equation is:

$$P(V_m - b) = RT$$

$$\Rightarrow Z = \left(1 + \frac{Pb}{RT}\right)$$

15. LIQUEFICATION OF GASES

When the molecules of a gas are brought closer to each other, due to increase in the attractive forces, a stage may be reached when the gas changes its phase to liquid. This phenomenon is called Liquefaction of gases.

15.1 Critical Temperature, T_C

The characteristic temperature of a real gas above which it cannot be liquefied.

$T_C = 8a/27Rb$

15.2 Critical Pressure, P_C

It is the minimum pressure required for liquefaction to take place at critical temperature

$P_C = a/27b^2$

15.3 Critical Volume, V_C

It is the volume occupied by one mole of a gas under critical temperature and pressure.

$V_C = 3b$

NB: *The compressibility factor at critical point is constant for all gases and has a value of 0.375.*

For liquefication of real gases, we can do either of the following :

(1) Increase the pressure on the gas

(2) Decrease the temperature of gas but temperature is the dominant factor and pressure assumes a secondary role.

16. LIQUID STATE

Intermolecular forces are stronger in liquid state than in gaseous state.

1. Properties of liquids : Molecules in liquids are so close that there is very little empty space between them and under normal conditions liquids are denser than gases.

2. Molecules of liquids are held together by attractive intermolecular forces. Liquids have definite volume because molecules do not separate from each other.

3. Molecules of liquids can move past one another freely, therefore, liquids can flow, can be poured and can assume the shape of the container in which these are stored.

4. **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.

Factors affecting vapour pressure

Two important factors on which the vapour pressure of a liquids depends are :

(a) **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 the vapour phase and hence the vapour pressure is higher.

(b) **Effect of temperature :** As the temperature of a liquid is increased, the vapour pressure of the liquid increases.

Boiling point of a liquid is defined as the temperature at which the vapour pressure of the liquid becomes equal to the external pressure (i.e., the atmospheric pressure).

When the external pressure is normal atmospheric pressure (i.e., 760 mm), the boiling point is called the normal boiling point.

When the external pressure is equal to 1 bar, the boiling point is called standard boiling point of the liquid.

Some Applications of Effect of External Pressure on Boiling point.

(i) Obviously, if the external pressure is higher, more heat will be required to make the vapour pressure equal to the external pressure and hence higher will be the boiling point. That is why in hospitals, surgical instrumnts are sterilized in autoclaves in which boiling point of water is raised by using a weight to cover the vent.

(ii) Similarly, 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 a mountain (where pressure is low) than on the sea shore. That is why at hills, use of pressure cooker is essential for cooking food.

5. **Surface tension** is a characteristic property of liquids which arises due to the fact that the molecules of the liquid at the surface are in different situation than those in the interior of the liquid.

Surface tension of a liquid is defined as the force acting at right angles to the surface along one centimetre length of the surface. Thus, the units of surface tension are dynes per cm (or Newtons per metre, i.e., N m^{-1} in the S.I. system.

Some important Results

(i) **Spherical shape of drops** the lowest energy state of a liquid will be when the surface area is minimum. Surface tension tries to decrease the surface area of the liquid to the minimum. The drops of a liquid (or the bubbles of a gas) are spherical because for a given volume, a sphere has minimum surface area.

(ii) **Fire polishing of glass.** Sharp glass edges are heated to make them smooth. This is because on heating, the glass melts and takes up rounded shape at the edges which has minimum surface area.

(iii) **Rise of a liquid in a capillary tube.** This rise is obviously due to the inward pull of surface tension acting on the surface which pushes the liquid into the capillary tube.

(iv) **Effect of nature of the liquid on surface tension.** Surface tension is a property that arises due to the intermolecular forces of attraction among the molecules of the liquid. Greater are the intermolecular forces of attraction, higher is the surface tension of that liquid.

(v) **Effect of temperature on surface tension.** The surface tension of liquids generally decreases with increase of temperature and becomes zero at the critical temperature (where the meniscus between the liquid and the vapour disappears). The decrease in surface tension with increase of temperature is obviously due to the fact that with increase of temperature, the kinetic energy of the molecules (and hence the speeds of molecules) increases and, therefore, the intermolecular attraction decreases.

6. **Viscosity** is one of the characteristic properties of liquids. Viscosity is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows.

The type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called laminar flow.

If the velocity of the layer at a distance dz is changed by a value du then velocity gradient is given by the amount $\frac{du}{dz}$.

A force is required to maintain the flow of layers. This force is proportional to the area of contact of layers and velocity gradient i.e.

$F \propto A$ (A is the area of contact)

$F \propto \frac{du}{dz}$ (where, $\frac{du}{dz}$ is velocity gradient; the change in velocity with distance)

$$F \propto A.\frac{du}{dz}$$

$$\Rightarrow\ F \propto \eta A\frac{du}{dz}$$

'η' is proportional constant and is called coefficient of viscosity. Viscosity coefficient is the force when velocity gradient is unity and the area of contact is unit area. Thus 'η' is measure of viscosity. SI unit of viscosity coefficient is 1 newton second per square metre (N s m^{-2}) = pascal second (Pa s = 1kg $m^{-1}s^{-1}$). In cgs system the unit of coefficient of viscosity is poise.

1 poise = 1 g $cm^{-1}s^{-1}$ = 10^{-1}kg $m^{-1}s^{-1}$

❖ Greater the viscosity, the more slowly the liquid flows. Hydrogen bonding and van der Waals forces are strong enough to cause high viscosity. Glass is an extremely viscous liquid.

❖ Viscosity of liquids decreases as the temperature rises because at high temperature molecules have high kinetic energy and can overcome the intermolecular forces to slip past one another between the layers.

17. MEASUREMENT OF PRESSURE OF A GAS

The pressure of a gas can be measured by various methods. Mostly it is measured in terms of heights of liquid column. We know that a liquid exerts pressure on the bottom of a container or a tube due to gravity.

Suppose there is a liquid of density ρ filled in a tube (cross sectional area A) up to a height h and there is vacuum above it.

Then :

Volume of the liquid = $\mathbf{A \times h}$

Mass of the liquid = $\boldsymbol{\rho \times A \times h}$

Force applied at the bottom = weight of the liquid = $\boldsymbol{\rho \times g \times A \times h}$

Pressure = F/A = ρgh

If a tube filled with a liquid is kept at an angle θ then only the vertical component of weight is taken.

Pressure = $\rho gh \times \sin\theta$

A common arrangement to measure pressure of a gas is called ***"Barometer"*** as shown in the figure.

A mercury barometer is used to measure atmospheric pressure by determining the height of a mercurry column supported in a sealed glass tube.

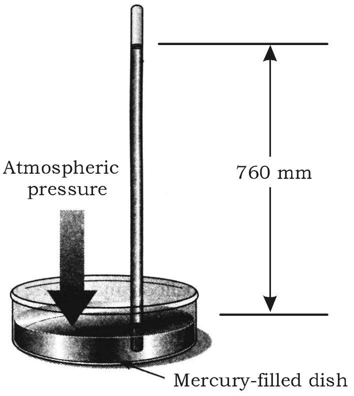


TABLE FOR FORMULAE USED IN THE CHAPTER

- For a U tube manometer; $\Delta h = \frac{P_1 - P_2}{\rho g}$
- **Boyle's Law :** $PV = \text{constant} \Rightarrow P_1V_1 = P_2V_2$
- **Charles' Law :** $V/T = \text{constant} \Rightarrow V_1/T_1 = V_2/T_2$
- **Gay Lussac's Law :** $P/T = \text{constant} \Rightarrow P_1/T_1 = P_2/T_2$
- **Avogadro's Law :** $V \propto n$
- **Ideal Gas Equation :** $PV = nRT$
- Variation of ideal gas equation: $PM = \rho RT$
- **Dalton's Law of Partial Pressure :** Pressure due a gas in a gas mixture $P_A = X_AP_{TOTAL}$
- **Graham's Law of diffusion :**

  rate of diffusion $\propto$ Pressure/ $\sqrt{\ }$
- $u_{RMS} = \sqrt{\frac{3RT}{\ }}$ $u_{MP} = \sqrt{\frac{2RT}{\ }}$

  $u_{AVG} = \sqrt{\frac{8RT}{\pi M}}$
- $u_{MP} : u_{AVG} : u_{RMS} = 1:1.128:1.224$
- **Compressibility Factor,** $Z = V_{real}/V_{ideal}$
- **Vander waal's Equation :**

  $\mathbf{(P+an^2/V^2)(V-nb) = nRT}$
- Vanderwaal's constant or co-volume:

  $b = 4\times(4/3\pi r^3)\, N_A$
- *At low/moderate pressure* $(P + an^2/V^2)\, V = nRT$

  and $\mathbf{Z = PV/nRT = 1 - \frac{an}{VRT}}$
- *At high pressure:* $P(V-nb) = nRT$ and

  $\mathbf{Z = (1+Pb/RT)}$
- *At very low pressure or at high temperature and moderate/low pressure:* $Z = 1$ and $PV = nRT$
- ***Critical Temperature :*** $\mathbf{T_c = 8a/27Rb}$
- ***Critical Pressure :*** $\mathbf{P_C = a/27b^2}$
- ***Critical Volume :*** $\mathbf{V_C = 3b}$

THERMODYNAMICS & THERMOCHEMISTRY

1. THERMODYNAMICS

It is the study of flow of energy. It encompasses the study of flow of heat as well as mass.

2. THERMODYNAMICS TERMINOLOGY

2.1 System

The part of the Universe under observation is called system.

2.2 Surrounding

The part of the Universe not under observation is called Surrounding.

System + Surrounding = Universe

2.3 Types of system

2.3.1 Open System : A system in which both flow of mass and heat is possible.

2.3.2 Closed System : A system in which flow of heat is possible but flow of mass is not possible.

2.3.3 Isolated System : A system in which neither heat nor mass can flow in or out.

3. STATE OF A SYSTEM

The state variables (P, V, T, n) describes the condition of a system. On changing any one or more of these variables the state of the system changes.

4. PROPERTIES OF SYSTEM

All the properties of a system can be categorized into one of the following two types :

4.1 Extensive Properties

Such properties of a system which depends on the mass or the total number of particles in the system are categorized as Extensive Properties. eg. Total Energy, volume.

4.2 Intensive Properties

Such properties of a system which depends on concentration and does not depend on the mass or the total number of particles in the system are categorized as Intensive properties. eg. Pressure, Density, Reractive Index.

5. STATE AND PATH FUNCTIONS

Such thermodynamic functions which depend only on the initial and final states of the system and not on the path followed are called **state functions** eg. Internal energy, Enthalpy and the functions which depend on the path followed while changing from one state to the other are called **path functions.** eg. work heat.

6. THERMODYNAMIC EQUILIBRIUM

A system is said to be under thermodynamic equilibrium when none of the state variables are changing and it satisfies the three equilibriums.

6.1 Mechanical Equilibrium

There is no mechanical motion and the pressure and the volume of the system is not changing.

6.2 Thermal Equilibrium

There is no flow of heat and the temperature of the system does not change with time.

6.3 Chemical Equilibrium

If any chemical reaction is taking place in the system then the rate of forward reaction is equal to the rate of backward reaction which means that the overall moles of the system is constant.

7. INTERNAL ENERGY

It is the sum total of the components of energy of the system due to the internal factors. It is denoted by U (sometimes by E). Since the system under observation is an ideal gas thus the internal energy of the system is dependent only on the kinetic energy of the gas and therefore is only a function of temperature. $\mathbf{U \propto T}$. Since internal energy depends only on temperature thus, it is a **state function.**

8. MODES OF ENERGY TRANSFER

There are two methods to alter the internal energy of a system viz. **Heat and work.**

8.1 Heat

Heat is the energy transferred due to temperature difference between the system and the surrounding. On heating, the kinetic energy of the molecules increases and therefore the internal energy increases.

8.2 Work

Work is the energy spent to overcome an external force. When the system does work against an external pressure (expansion) it tends to reduce the internal energy and on the other hand when the system contracts due to the external pressure it tends to increase the internal energy.

9. FIRST LAW OF THERMODYNAMICS

The first law of Thermodynamics states that Energy can neither be created nor destroyed.

$\Delta U = q + w$

Conventions : In the above system if work is done by the system then w is negative and if work is done on the system then w is positive. Also, if heat flows into the system then q is positive and if heat flows out of the system then q is negative.

10. REVERSIBILITY

A process whose direction can be changed by an infinitesimal change to the system or surroundings and which can be reversed by retracing the original path and the system is restored to the initial state. The driving force of a reversible process is very-very small and such a process is extremely slow. For a process to be reversible there must not be any dissipative forces and also the system should be in a Quasi Static State.

10.1 Quasi Static State

A quasi static state means that the system seems to be static at all intervals of time but actually is not. The motion is so slow that it is almost impossible to detect the motion and the system seems to be in equilibrium with the surroundings at all instants of time.

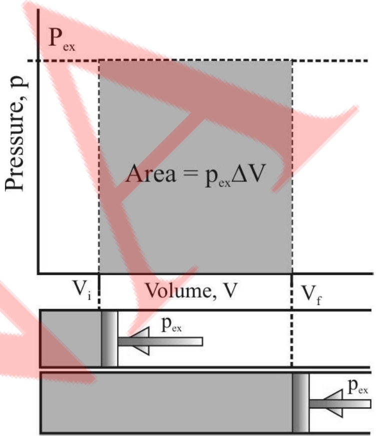
11. EXPANSION WORK

It is the work done due to the volume changes of the gas. The mathematical expression for the expansion work is $w = -\int P_{ex} dV$.

Always remember, be it expansion or compression we always take the external pressure as the driving force. For a reversible process,

$P_{ex} \approx P_{GAS}$ and $w = -\int P_{GAS} dV$.

If we draw a process curve between P and V then the work done is represented by the area covered under the P-V graph as shown in Fig.



NOTE

Sign of w : If the volume of the system is increasing then the sign of **w is –ve** and if volume is decreasing **w is +ve**

Sign of ΔU : If the temperature of the system is decreasing or the product pressure and volume (PV) is reducing then the sign of **ΔU is –ve** else, the sign of **ΔU is +ve.**

Sign of q : The sign of q needs to be determined using the first law of thermodynamics.

12. CYCLIC PROCESS

A cyclic process is one which comes back to its initial state. The graph of a cyclic process is always a closed graph. For a cyclic process, $\Delta U_{net} = 0$ and $q_{net} = -w_{net}$.

13. ENTHALPY (H)

Enthalpy is another thermodynamic function (like internal energy, work and heat) which we study in various thermodynamic processes. It is also a state function like internal energy. It is defined as the sum of the energy stored in the system and the energy used in doing work. Mathematically, $H = U + PV$. At constant pressure $\Delta H = q_p$ and at constant volume $\Delta U = q_V$.

14. HEAT CAPACITY (C)

The heat capacity of the system is the amount of heat needed to raise the temperature of the system by 1°C or 1K.

$\mathbf{C = q/\Delta T.}$

14.1 Molar Heat Capacity

The **molar heat capacity** of a system (C_M) is the amount of heat needed to raise the temperature of one mole gas by 1°C or K.

$$C_M = \frac{q}{n\Delta T}$$

The **molar heat capacity of a system at constant pressure** (C_p) is the amount of heat needed to raise the temperature of one mole gas the system by 1°C at constant pressure.

$\mathbf{C_p = q_p/n\Delta T.}$

The **molar heat capacity of a system at constant volume** (C_V) is the amount of heat needed to raise the temperature of one mole gas by 1°C at constant volume.

$\mathbf{C_V = q_V/n\Delta T.}$

Thus, we can say that : $\Delta H = nC_P\Delta T$ and $\Delta U = nC_V\Delta T$ and $C_P = C_V + R$.

Type of Gas	C_V	C_P	$\gamma = C_P/C_V$
monotomic	3R/2	5R/2	5/3 = 1.67
diatomic	5R/2	7R/2	7/5 = 1.4
Non-linear Polyatomic	3R	4R	4/3 = 1.34

15. TYPES OF THERMODYNAMIC PROCESSES

There are four important types of processes to be studied in this chapter. The basic meanings and difference of these four processes are :

15.1 Isothermal Process

These processes are the ones in which the temperature is constant throughout the process.

$\mathbf{\Delta U = 0; \quad \Delta H = 0}$

$\mathbf{w = -2.303\ nRT \log_{10}(V_2/V_1) = -\ 2.303\ nRT \log_{10}(P_1/P_2)}$

$\mathbf{q = +2.303\ nRT \log_{10}(V_2/V_1) = +\ 2.303\ nRT \log_{10}(P_1/P_2)}$

15.2 Adiabatic Process

These processes are the ones in which the heat exchanged with the surroundings is zero. Such processes are defined by the equation

$\mathbf{TV^{\gamma-1} = constant,\ \ T^{\gamma}P^{1-\gamma} = constant,\ \ PV^{\gamma} = constant.}$

$\mathbf{q = 0 \quad \Rightarrow \quad w = \Delta U}$

$\Delta U = nC_V\Delta T = (P_2V_2 - P_1V_1)/(\gamma - 1). = (nR\Delta T)/(\gamma - 1)$

$\Delta H = nC_P\Delta T$

15.3 Isochoric Process

These processes are the ones in which the volume remains constant. Since the change in volume is zero therefore we can say that

$\mathbf{w = 0}$

$\Delta U = nC_V\Delta T = q_V \qquad \Delta H = nC_P\Delta T$

15.4 Isobaric Process

These are the processes in which the pressure remains constant.

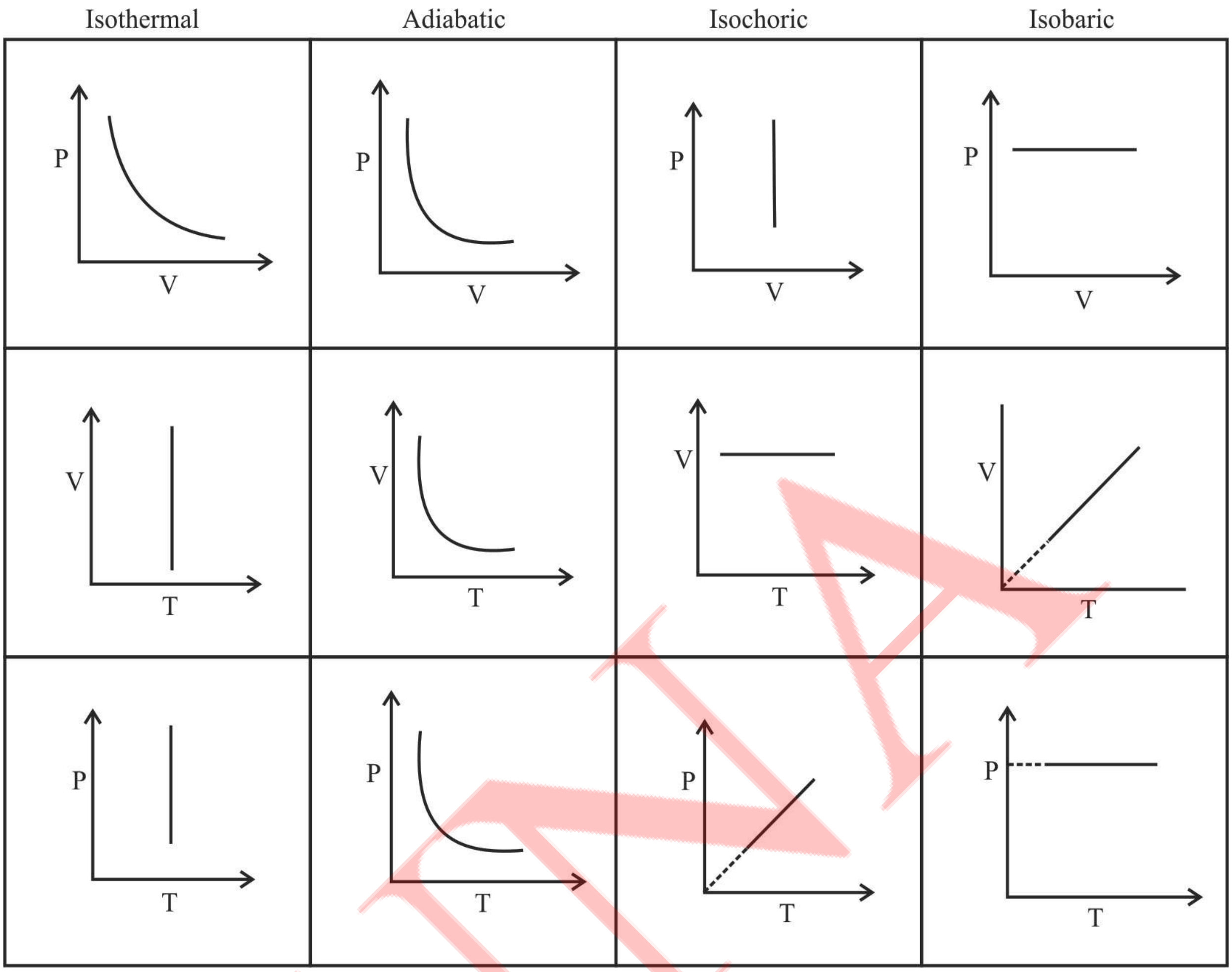
$\mathbf{w = -\ P\Delta V = -\ nR\Delta T}$

$\mathbf{\Delta U = nC_V\Delta T}$

$\mathbf{\Delta H = nC_P\Delta T}$

NOTE

All these processes are happening on a system containing an ideal gas therefore we can apply PV = nRT at any stage that we find suitable.



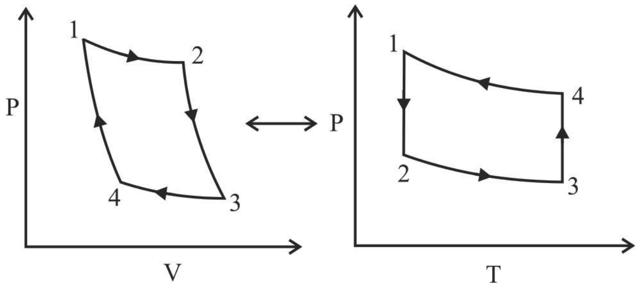
NOTE

Although the graph of isothermal and adiabatic processes are similar in nature it should be noted that the P-V graph of an adiabatic process is steeper than that of an isothermal process.

16. GRAPH TRANSFORMATION

When a thermodynamic process is plotted in terms of two state variable it can be transformed into a graph involving the other state variable by doing the following :

1. Identify the type of curve given, whether it is P-V, V-T or P-T graph.
2. Then, Identify every step of the process
3. Then one by one convert every step into the required graph bearing in mind critical points like, an expansion process will remain an expansion process and so on.
4. A cyclic process should remain cyclic whichever graph we make.



Note : From the given P–V graph.

Process 1→2 is isothermal expansion; 2→3 adiabatic expansion; 3→4 isothermal compression & 4→1 adiabatic compression.

17. IRREVERSIBLE PROCESS

For an irreversible process the work done is given by $W = -\int P_{EXT}dV$. We cannot take the external pressure to be equal to the pressure of the gas in these processes.

18. FREE EXPANSION

If the external pressure of the gas is zero that is the gas is expanding against vaccum then the work done is always zero, this is called the case of free expansion. In this process the gas does no work as there is no effort put in expansion process. If no heat is supplied to the gas then there is no change in temperature too. That is why such a process is both Isothermal and Adiabatic.

19. POLYTROPIC PROCESS

It is a generalized form of any thermodynamic process which has a form **PV^n = constant** where n is a real number. For an isothermal process n = 1 and for an adiabatic process $n = \gamma$. The heat capacity of a polytropic process can be calculated using the first law of thermodynamics and comes out to be :

$C = C_V - R/(n-1)$.

20. NEED FOR SECOND LAW

The first law talks about the conservation of energy in a process but does not speak of the feasibility of a process. It does not tell whether a process will happen on its own i.e. whether the process is spontaneous or not. A spontaneous process is one which happens on its own. Example, heat always flows spontaneously from higher temperature to lower temperature : Nothing in the first law mentions that the opposite process cannot happen. According to first law any process where energy remains conserved is feasible. But we need some other basis for feasibility of a process. This is where the second law is important.

21. TYPES OF PROCESSES

21.1 Spontaneous processes

Spontaneous processes have a natural tendency to take place and no external work is needed to carry out these processes. All natural processes are spontaneous.

21.2 Non-Spontaneous processes

They are driven by external work and cannot take place naturally.

22. CONCEPT OF ENTROPY

- Matter has a natural tendency to get disordered or randomised
- Energy has a tendency to become disordered or dispersed.

It was concluded that any such process in which the total randomness of the universe (system + surrounding) increases is a spontaneous process. **Entropy is a measure of randomness or disorder.** It is a state function represented by S. We can safely say that in a spontaneous process there is a tendency for increase in entropy. Hence the statement of second law :

The entropy of an isolated system/Universe tends to increase OR In a spontaneous process the entropy of the Universe increases.

$\Delta S = q_{rev}/T$.

$$\Delta S_{TOTAL} = \Delta S_{SYSTEM} + \Delta S_{SURROUNDING} > 0$$

(for a sponataneous change)

Thus, **In a reversible process the entropy of the Universe remains constant i.e. $\Delta S_{Total} = 0$**

22.1 Entropy changes in a Thermodynamic Process

The entropy changes in an thermodynamic process can be mathematically calculated by the equation :

$\Rightarrow \Delta S = nC_V \, ln\,(T_2/T_1) + nR \, ln\,(V_2/V_1)$. This expression can be simplified for the four processes studied earlier as :

Isothermal process : $\Delta S = nR \, ln\,(V_2/V_1)$

Isochoric process : $\Delta S = nC_V \, ln\,(T_2/T_1)$

For isobaric process : $\Delta S = nC_P \, ln\,(T_2/T_1)$

Adiabatic process : $\Delta S = 0 \; (q_{rev} = 0)$

22.2 Important points to Remember

1. Entropy of a system remains constant in a reversible adiabatic process. Therefore, it is also known as **"isentropic process".**
2. Entropy of an ideal gas will always increase in isothermal expansion.
3. In a reversible adiabatic process the entropy of both system and surroundings remains the same and there is no overall change in entropy as well.

$$\Delta S_{SYSTEM} = \Delta S_{SURROUNDINGS} = \Delta S_{TOTAL} = 0$$

4. In a reversible isothermal expansion the entropy of surroundings will always decrease to balance the increase in system's entropy to make the overall entropy constant.
5. In free expansion the entropy of the system always increases and that of surrounding remains constant. Free expansion is both isothermal and adiabatic and is irreversible.

23. GIBB'S FREE ENERGY

Gibb's Free energy function gives us a very convenient parameter to judge the spontaneity of a process from system's perspective. At a constant temperature and pressure, $\Delta G = -T\Delta S_{TOTAL}$ and for a process to be spontaneous, $\mathbf{\Delta G < 0}$. The change in Gibb's free energy can also be represented in terms of the system parameters as :

$\Delta G_{SYS} = \Delta H - T\Delta S_{sys}$ at a constant temperature.

24. THERMOCHEMICAL EQUATION

A chemical equation which gives us all the information like energy changes associated with a chemical reaction and phases of various reactants and products is called Thermochemical Equation.

All reactions can be categorized into one of the following two categories :

24.1 Endothermic Reactions

Are those chemical reactions which absorb energy.

(ΔH = positive)

24.2 Exothermic Reactions

Are those chemical reactions which release energy.

(ΔH = negative)

For a chemical reaction, $\Delta H_{REACTION} = H_{PRODUCTS} - H_{REACTANTS}$

The change in enthalpy during a chemical reaction occurs due to breaking and making of bonds.

Also, $\Delta H = \Delta U + \Delta n_g RT$.

25. ENTHALPY OF REACTIONS

Enthalpy change can be calculated for all reactions and is sometimes called the Heat of Reaction. Let's take a look at various types of reactions and enthalpy changes associated with them :

25.1 Enthalpy of Formation ΔH_f^0

It is the heat absorbed or released when one mole of a compound is formed from its constituent elements under their standard elemental forms. The enthalpy for formation of the following substances is taken to be zero under 1 bar pressure and 298 K.

$\Delta H_f^0 (O_2, g) = 0$ $\qquad$ ΔH_f^0 (S, Rhombic) = 0

ΔH_f^0 (C, graphite) = 0 $\qquad$ ΔH_f^0 (P, white) = 0

$\Delta H_f^0 (Br_2, l) = 0$ $\qquad$ $\Delta H_f^0 (H^+, aq) = 0$

25.2 Enthalpy of Combustion

It is the heat released or absorbed when one mole of a substance undergoes combustion in presence of oxygen.

$$CH_4 (g) + 2O_2 (g) \rightarrow CO_2 (g) + 2H_2O (g) \quad \Delta H = -890 \text{ kJ/mol}$$

25.3 Enthalpy of Solution

It is the heat released or absorbed when 1 mole of a compound is dissolved in excess of a solvent (water).

$$MgSO_4 (s) + H_2O \text{ (excess)} \rightarrow Mg^{2+} (aq) + SO_4^{2-} (aq)$$

$$\Delta H^0_{Sol} = -91.211 \text{ kJ/mol}$$

25.4 Enthalpy of Hydration

It is the energy released or absorbed when 1 mole of anhydrous or partially hydrated salt undergoes hydration by the addition of water of crystallisation. e.g.

$$CuSO_{4(s)} + 5H_2O_{(l)} \rightarrow CuSO_4 . 5H_2O(s)$$

$$\Delta H_{HYD} = -78.9 \text{ kJ/mol}$$

25.5 Enthalpy of Neutralization

It is the heat released or absorbed when one equivalent of an acid undergoes neutralisation with one equivalent of a base. e.g.

$H^+(aq) + OH^-(aq) \rightarrow H_2O\,(l)$

$\Delta H_R = -57.3$ kJ/mol

26. HESS LAW OF CONSTANT HEAT SUMMATION

Since enthalpy is a state function thus for a reaction which takes place in steps the net change in enthalpy can be calculated by adding the enthalpy changes of each step. This is called the **Hess Law.**

27. BORN HABER CYCLE

The entire thermodynamics process of formation of an ionic crystal lattice is called Born Haber cycle. An ionic compound is formed from its constituents through a series of steps involving conversion of atoms/molecules into gaseous phase for ion formation, ionisation and electron gain to form ions and then the reaction of gaseous ions to form solid lattice.

28. BOND DISSOCIATION ENTHALPY

The energy needed to break the bonds of one mole molecules is called the Bond Dissociation Enthalpy of the substance. It is defined per mol of molecule. eg. Bond dissociation enthalpy of H_2 is 436 kJ/mol

29. HEAT OF ATOMIZATION

It is defined as the energy required to convert any substance to gaseous atoms. This is defined per mol of the gaseous atoms. For example Heat of atomisation of H will be 218 kJ/mol atoms.

30. RESONANCE ENERGY

Many compounds exhibit resonance. Due to resonance they exist in a structure which is different from the expected one and more stable.

Resonance energy $= \Delta H^0_f(\text{actual}) - \Delta H^0_f(\text{calculated})$

CHEMICAL EQUILIBRIUM

1. INTRODUCTION

Equilibrium represents the state of a process in which the proprties like temperature, pressure, concentration of the system do not show any change with the passage of time.

If the opposing processes involve only physical changes, the equilibrium is called physical equilibrium. If the opposing processes involve chemical changes, i.e., the opposing processes are chemical reactions, the equilibrium is called chemical equilibrium.

2. EQUILIBRIA IN CHEMICAL PROCESSES

2.1 Reversible Reactions

A reaction in which not only the reactants react to form the products under certain conditions but also the products react to form reactants under the same conditions is called a reversible reaction. In other words a reaction which takes place not only in the forward direction but also in the backward direction under the same conditions is called a reversible reaction.

A reversible reaction between A and B to form C and D is represented as :

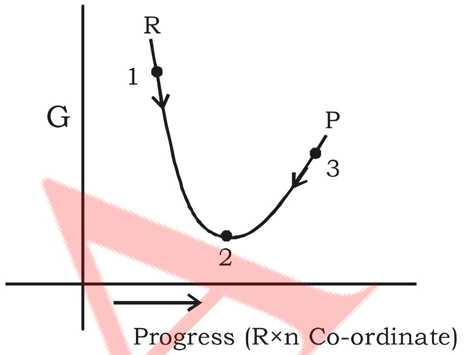
$$A + B \rightleftharpoons C + D$$

2.2 Irreversible Reactions

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, it is called an irreversible reaction.

$$A + B \longrightarrow C + D$$

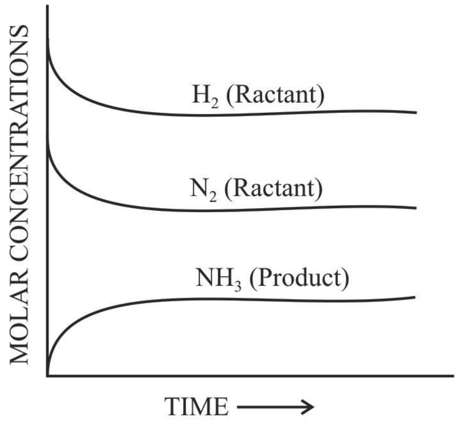
2.3 Concept of Chemical Equilibrium



- It is the state of minimum Gibb's energy
- $dG = 0$ and $\Delta G = 0$ at this state
- Rate of forward reaction = Rate of backward reaction
- This equilibrium is dynamic and stable in nature

Dynamic Nature of Chemical Equilibrium

In the Haber's process, starting with definite amounts of N_2 and H_2 and carrying out the reaction at a particular temperature, when equilibrium is attained, the concentrations of N_2, H_2 and NH_3 become constant. If the experiment is repeated by taking deuterium (D_2) in place of H_2 but with the same amounts and exactly similar conditions as before, equilibrium is attained containing D_2 and ND_3 in place of H_2 and NH_3 but in the same amounts. Now, if the two reaction mixtures are mixed, then after some time, it is found that the concentrations of ammonia and hydrogen are same except that now all forms of ammonia (i.e., NH_3, NH_2D, NHD_2, ND_3) and all forms of hydrogen (i.e., H_2, HD, $_2$) are present. This shows that at equilibrium, the reaction is still going on, i.e., equilibrium is dynamic in nature.



Representing the attainment of equilibrium for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons NH_3(g)$

2.4 Characteristics of Chemical Equilibrium

(i) At equilibrium, the concentration of each of the reactants and the products becomes constant.

(ii) At equilibrium, the rate of forward reaction becomes equal to the rate of backward reaction and hence the equilibrium is dynamic in nature.

(iii) A chemical equlibrium can be established only if none of the products is allowed to escape out or separate out as a solid.

e.g. if CO_2 gas escapes out in case of decomposition of CaCO , the reaction will no longer remain reversible.

Similarly, the reaction is irreversible if one of the products separates out as solid,

$$AgNO_3 + KCl \longrightarrow AgCl\downarrow + KNO$$

(iv) Chemical equilibrium can be attained from either direction, i.e., from the direction of the reactants as well as from the direction of the products.

3. RATE OF A REACTION

Average Rate = Change in concentration/Time taken = $\Delta c/\Delta t$

Δc = Final Concentration – Initial concentration

3.1 Instantaneous rate

Lim $\Delta c/\Delta t = dc/dt$

$\Delta t \to 0$

Units of rate : conc/time or mol/Ls

3.2 Overall rate of a reaction

$\mathbf{aA + bB \leftrightarrow cC + dD}$

Overall Rate =

$-(1/a)\,\Delta A/\Delta t = -(1/b)\,\Delta B/\Delta t = +(1/c)\,\Delta C/\Delta t = +\,(1/d)\,\Delta D/\Delta t$

Overall rate :

Rate of forward reaction – Rate of backward reaction

"At equilibrium the overall rate of a reversible reaction becomes zero".

4. EQUILIBRIUM CONSTANT (K)

4.1 Law of Mass Action

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.

$$aA + bB + cC + \ldots\ldots \longrightarrow \text{Products}$$

$$\text{Rate of reaction} \propto [A]^a\,[B]^b\,[C]^c\,\ldots\ldots$$

Law of Chemical Equilibrium is a result obtained by applying the Law of Mass Action to a reversible reaction in equilibrium.

$$A + B \rightleftharpoons C + D$$

Rate of the forward reaction $\propto [A]\,[B] = k_f[A]\,[B]$

Rate of the backward reaction $\propto [C]\,[D] = k_b\,[C]\,[D]$

At equilibrium,

Rate of forward reaction = Rate of backward reaction

$$k_f[A][B] = k_b\,[C][D] \quad \text{or} \quad \frac{[C][D]}{[A][B]} = \frac{k_f}{k_b} = K$$

At constant temperature, as k_f and k_b are constant, therefore,

$\frac{k_f}{k_b}$ = K is also constant at constant temperature and is called 'Equilibrium constant'.

The product of the molar concentrations of the products, each raised to the power equal to its stoichiometric coefficient divided by the product of the molar concentrations of the reactants, each raised to the power equal to its stoichiometric coefficient is constant at constant temperature and is called Equilibrium constant.

4.2 Characteristics of Equilibrium Constant

(i) The value of the equilibrium constant for a particular reaction is always constant depending only upon the temperature of the reaction and is independent of the concentrations of the reactants with which we start or the direction from which the equilibrium is approached.

(ii) If the reaction is reversed, the value of the equilibrium constant in inversed.

(iii) If the equation (having equilibrium constant K) is divided by 2, the equilibrium constant for the new equation is the square root of K (i.e., $\sqrt{K}$).

(iv) If the equation (having equilibrium constant K) is multiplied by 2, the equilibrium constant for the new equation is the square of K (i.e., K^2)

(v) If the equation (having equilibrium constant K) is written in two steps (having equilibrium constant K_1 and K_2) then $K_1 \times K_2 = K$.

(vi) The value of the equilibrium constant is not affected by the addition of a catalyst to the reaction.

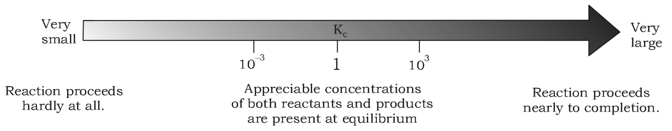
This is because the catalyst increases the speed of the forward reaction and the backward reaction to the same extent.

4.3 Extent of Reaction

High value of Kc **($K_c > 10^3$)** → At equilibrium reaction is forward dominant

Low value of Kc **($K_c < 10^{-3}$)** → At equilibrium reaction is backward dominant

Moderate value of K_c **(between 10^3 and 10^{-3})** → At equilibrium neither direction dominates



4.4 Reaction Quotient (Q)

$aA + bB \leftrightarrow cC + dD$

$Q = [C]^c [D]^d / [A]^a [B]^b$

$Q > K_c$: Reaction will tend towards backward direction

$Q > K_c$: Reaction will tend towards forward direction

$Q > K_c$: Reaction will be at equilibrium

Note :

Q is a variable which always approaches K_{eq} which is a constant.

4.5 Calculating Equilibrium Concentrations

Suppose we are given the following data :

1. The balanced reaction and value of K_c
2. The initial concentration of the reactants, or the initial moles
3. Volume of the container

And we need to find the final equilibrium concentration of the reactants and products. Then we can follow the following steps :

Step-1

Write down the balanced chemical equation for the reaction

Step-2

Under every reactant and product, write down the initial moles/concentration

Step-3

Subtract the amount reacting and add the amount produced in terms of a variable x and note down the equilibrium concentration in terms of x. If we are dealing in moles then we will need to divide the moles by volume to obtain concentrations.

Step-4

Substitute the equilibrium concentration in the expression of K_c and equate it to the value of K_c.

Step-5

Solve the above equation and calculate the value of x and in case of multiple solutions select the value which is sensible from reaction point of view. Then back substitute the value of x in the equilibrium concentration expression and obtain the actual value of the same.

4.6 Equilibrium constant K_p

$aA + bB \leftrightarrow cC + dD$

$K_p = (P_C^c \times P_D^d)/ (PAa \times P_B^b)$

where P_C, P_D, P_A, P_B are partial pressures of A, B, C and D respectively.

$K_p = K_c (RT)^{\Delta n}$

R = 0.0821 L atm/mol–K

4.7 Relationship of K_{eq} and ΔG

For any reaction :

$\Delta G = \Delta G^o + RT\ InQ$ Where Q is the reaction quotient.

At equilibrium $\Delta G = 0$

$\Delta G^o = -RT \ln K_{eq} = -2.303RT \log_{10} K_{eq}$

where K_{eq} is generally taken as K_p. It depends on the definition of standard values to define ΔG^o.

If the standard active masses are taken as 1 M each then we will take $K_{eq} = K_C$ and if they are taken as 1 atm each then we will take $K_{eq} = K_p$.

4.8 Dependence of K_{eq} on temperature

Van't Hoff Equation :

$\ln (K_2/K_1) = (\Delta H/R)\ (1/T_1 - 1/T_2)$ or

$\log 10\ (K_2/K_1) = (\Delta H/2.303R)\ (1/T_1 - 1/T_2)$

Exothermic Reactions

ΔH = negative

On increasing the temperature the equilibrium constant will decrease i.e. The reaction will become more backward dominant.

Endothermic Reaction

ΔH = possitive

On increasing the temperature the equilibrium constant will increase. The reaction will become more forward dominant.

POINTS TO REMEBER

Whether the reaction is exothermic or endothermic on increasing the temperature, it will tend towards endothermic direction.

5. HOMOGENOUS EQUILIBRIA

Reactions in which all reactants and products are in the same phase Homogenous Reactions can further be divided into three sub-categoreis :

5.1 Those reactions where gaseous moles increase (Δn = +ve)

$PCl_5 (g) \leftrightarrow PCl_3 (g) + Cl_2 (g)$

5.2 Those reactions where gaseous moles remain the same ($\Delta n = 0$)

$H_2 (g) + I_2 (g) \leftrightarrow 2HI (g)$

5.3 Those reactions where gaseous moles decrease (Δn = – ve)

$2NO_2 (g) \leftrightarrow N_2O_4 (g)$

6. DEGREE OF DISSOCIATION, α

It is defined as the fraction of molecules dissociating. For example, if 100 molecules are present and only 40 dissociate then the degree of dissociation is 0.4 or 40%.

7. HETEROGENEOUS EQUILIBRIA

Category of reactions where various phases/states exist in the same reaction.

In presence of gases the activity of solids and excess liquids is constant. Therefore we can assume the active masses of solids and excess liquids as constant.

$CaCO_{3(s)} \leftrightarrow CaO_{(s)} + CO_{2(g)}$

$K_c = [CO_2]$

$Kp = P_{CO_2}$

8. LE CHATELIER'S PRINCIPLE

If a distrubance is introduced in an equilibrium mixture it will behave so as to undo the distrubance and re-establish equilibrium.

8.1 Effect of Change of Concentration

If in a reaction in equilibrium, the concentration of any reactant is increased, the equilibrium shifts in the forward direction. On the other hand, if the concentration of any product is increased, the equilibrium shifts in the backward direction. The reverse happens if the concentrations are decreased.

8.2 Effect of change of temperature

Exothermic reactions are favoured by low temperature whereas endothermic reations are favoured by high temperature.

8.3 Effect of change of pressure

Low pressure favours those reactions which are accompanied by increase in total number of moles and high pressure favours those reactions which take place with decrease in total number of moles. However, pressure has no effect on an equilibrium reaction which proceeds with no change in total number of moles.

8.4 Effect of change in volume

The effect of decrease of volume is equivalent to the effect of increase of pressure.

hence the effect of decrease in volume will be to shift the equilibrium in the direction in which the number of moles decreases.

8.5 Effect of a Catalyst

A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products. It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium. Catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression.

eg contact process,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g);\ K_c = 1.7 \times 10^{26}$$

Practically the oxidation of SO_2 to SO_3 is very slow. Thus, platinum or divanadium penta-oxide (V_2O_5) is used as catalyst to increase the rate of the reaction.

8.6 Effect of adding an inert gas to a reaction mixture in equilibrium.

(a) If the reaction takes place at constant volume addition of an inert gas will not change the molar concentrations of the reactants and products. Hence, the state of equilibrium will remain unaffected.

(b) If the reaction takes place at constant pressure, addition of inert gas must accompany in increase in the total volume to keep pressure constant. Thus, reaction shifts towards larger number of moles.

IONIC EQUILIBRIUM

Ionic equilibrium is the study of equilibrium in the reactions where formation of ions take place in aqueous solution.

1. ELECTROLYTES

Electrolytes are those compounds which on dissolving in polar solvents like water break into ions. The solution of electrolytes conducts electricity because of the presence of ions.

1.1. Classification of electrolytes

1.1.1 Electrolytes can be classified on the basis of their strength into two categories:

Strong electrolytes : Those electrolytes which easily break into ions and give almost complete dissociation. Eg. HCl, NaOH, NaCl, HNO_3, $HClO_4$, H_2SO_4, $CaCl_2$ etc

Weak electrolytes : Those electrolytes which dissociate partially. Eg. CH_3COOH, NH_4OH, HCN, $H_2C_2O_4$, and all organic acids and bases etc.

1.1.2 Electrolytes can be further classified on the basis of the kind of compound they are.

- **Acids**
- **Bases**
- **Salts**

1.2 Acids and Bases

The definition of acids and bases varies from theory to theory:

1.2.1 Arrhenius theory

This theory defines acids and bases from the perspective of water as a solvent.

Arrhenius acids: Those compounds which will increase H^+ ion concentration in water. Eg HCl, H_2SO_4, CH_3COOH etc

$$HA \leftrightarrow H^+ + A^-$$

Arrehenius bases: Those compounds which will increase OH^- ion concentration in water. Eg. NaOH, $Ca(OH)_2$, NH_4OH etc

The major drawback of this theory is that the basis of all definitions is water.

$$BOH \leftrightarrow B^+ + OH^-$$

1.2.2 Bronsted-Lowry concept

Acids : Those compounds which can transfer protons that is H^+ to other compounds

Bases: Those compounds which can accept protons.

That is, Bronsted acids are "proton donors" and Bronsted bases are "Proton acceptors".

$$\underset{\textbf{Acid-1}}{HCl} + \underset{\textbf{Base-1}}{H_2O} \leftrightarrow \underset{\textbf{Acid-2}}{H_3O^+} + \underset{\textbf{Base-2}}{Cl}$$

Conjugate Acid-Base pairs: Pairs which are separated by a proton and exhibit opposite behaviours in the two directions of the same reaction. Eg. In the above reaction HCl and Cl^- are conjugate acid-base pairs.

Note : In a conjugate pair if acid is strong the base is weak and vice-versa.

1.2.3 Lewis Concept

Acid: A compound which can accept a pair of electrons.

Base: is a compound which can transfer its lone pair of electrons.

Eg. $BF_3 + NH_3 \leftrightarrow H_3N \rightarrow BF_3$

In the above reaction BF_3 is a lewis acid and NH_3 is a lewis base.

2. DISSOCIATION OF WEAK ACIDS AND BASES

$$HA \leftrightarrow H^+ + A^-$$

$K_a = c\alpha^2/(1 - \alpha)$

K_a is called "ionisation constant" or the "Dissociation constant" of the acid.

For low dissociation : $1 - \alpha \approx 1$

$K_a = c\alpha^2$

$\Rightarrow \alpha = \sqrt{(K_a / C)}$ This expression will be valid only when $\alpha < 0.05\ (5\%)$

$[H^+] = c\alpha = \sqrt{cK_a} = [A^-]$

Similarly for a Weak base $K_a = c\alpha^2/(1-\alpha)$

K_b is called "ionisation constant" or "dissociation constant" for the base.

$\alpha = \sqrt{(K_b / C}$ This expression will be valid only when $\alpha < 0.05\,(5\%)$

$[B^+] = [OH^-] = \sqrt{cK_b}$

Note :

α weak electrolytes increase on dilution

3. SELF-IONISATION OF WATER

$H_2O \leftrightarrow H^+ + OH^-$

$K_w = [H^+][OH^-]$

K_w is called ionic product of water.

For pure water: $[H^+] = [OH^-]$

At 25° C we know that $[H^+][OH^-] = 10^{-14}$

$[H^+] = [OH^-] = \sqrt{K_w} = 10^{-7}\,M$

Acidic: $[H_3O^+] > [OH^-]$

Neutral: $[H_3O^+] = [OH^-]$

Basic: $[H_3O^+] < [OH^-]$

Note: K_w increases as temperature increases.

4. pH SCALE

$pH = -\log_{10}[H^+]$

$pH + pOH = pK_w = 14$ (at 25°)

At 25°C

$pH < 7$ Acidic

$pH > 7$ Basic

$pH = 7$ Neutral

5. MIXTURE OF TWO WEAK ACIDS

$[H^+] = (x + y) = \sqrt{c_1K_1 + c_2K_2}$

6. BUFFER SOLUTIONS

Solutions which can resist any change in pH on addition of small amount of acid or base.

Buffer solutions are of three types:

6.1 Acidic Buffer Eg.

$CH_3COOH + CH_3COONa$

Henderson-Hasselbalch equation

$pH = pK_a + \log [salt]/[acid]$

6.1.1 Buffer Range:

$pK_a - 1 \le pH \le pK_a + 1$

6.2 Basic Buffer Eg.

NH_4OH and NH_4Cl

$pOH = pK_b + \log [salt]/[base]$

6.2.1 Buffer range:

$pK_b - 1 \le pOH \le pK_b + 1$

6.3 Mixed Buffer Eg.

CH_3COONH_4

Note :

- pH of a buffer solution does not change on dilution.
- For any acid-conjugate base pair $K_a.K_b = K_w$

7. POLYPROTIC ACIDS

Those acids which can furnish more than one H^+ permolecule. Eg. H_2SO_4, H_2CO_3, H_3PO_4

For any polyprotic acid : $\mathbf{K_1 > K_2 > K_3}$ **....so on**

For dissociation of H_2A $\quad \mathbf{[A2^-] \approx K}$

i.e. The concentration of the second ion of a polyprotic acid is almost equal to the second dissociation constant.

8. SALT HYDROLYSIS

Depending on the nature of the parent acid and base there can be 4 type of salts:

8.1 Salt of strong acid and strong base (NaCl)

This type of salt do not get hydrolysed.

Neutral solution with pH = 7

8.2 Salt of weak acid and strong base (CH_3COONa)

This type of salt give acidic solution on hydrolysis.

$K_h = C\alpha_h^2/(1 - \alpha_h) = K_w/K_a$; $pH = 7 + ½\, pK_a - ½ \log C$

8.3 Salt of Strong acid and weak base (NH_4Cl)

This type of salt give basic solution on hydrolysis.

$K_h = C\alpha_h^2/(1 - \alpha_h) = K_w/K_b$; $pH = 7 - ½\, pK_b - ½ \log C$

8.4 Salt of weak acid and weak base (CH_3COONH_4)

This type of salt may give acidic,basic or neutral solution.

$K_h = \alpha_h^2/(1 - \alpha_h)^2 = K_w/(K_a \times K_b)$; $pH = 7 + ½\, pK_b - ½\, pK_b$

9. SPARINGLY SOLUBLE SALTS & PRECIPITATION

When a salt is dissolved in water then it starts breaking into ions and after sometime the solubility process attains equilibrium.

$AgCl_{(s)} \leftrightarrow Ag^+_{(aq)} + Cl^-_{(aq)}$

$K_{sp} = [Ag^+]\,[Cl^-] = Q = I.P.$

$I.P. < K_{sp} \Rightarrow$ forward reaction, more salt can be dissolved

$I.P. = K_{sp} \Rightarrow$ saturation, no more salt can be dissolved

$I.P. > K_{sp} \Rightarrow$ backward reaction, precipitation of solid salt will take place