TEACHING / TRAINING MODULE

CHEMISTRY

CLASS - XI & XII

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FOREWORD

The ST and SC Development Department, Government of Odisha, has initiated an innovative effort by setting up an ***Academic Performance Monitoring Cell*** (APMC) in Scheduled Castes and Scheduled Tribes Research and Training Institute (SCSTRTI) to monitor the Training and Capacity Building of teachers of SSD Higher Secondary Schools and Ekalabya Model Residential Schools (EMRS) under the administrative control of the ST & SC Development Department. This innovative program is intended to ensure quality education in the Higher Secondary Level of the schools of the ST & SC Development Department.

The modules and lesson plans are prepared for the +2 Science and Commerce stream' in all the subjects such as Physics, Chemistry, Botany, Zoology, Mathematics, Information Technology, Odia, English and Commerce for both the years in line with the syllabus of Council of Higher Secondary Education (CHSE).

These modules/lesson plans are self contained. The subiect experts who are the best in their respective subjects in the State have been roped in for the exercise. They have given their precious time to make the module as activity based as possible.

I hope, this material will be extremely useful for the subject teachers in effective class room transactions and will be helpful in improving the quality education at the Higher Secondary Level. I also take this opportunity to thank all the subject experts of different subjects for rendering help and assistance to prepare the modules/lesson notes and lesson plans within a record time.

Prof. (Dr.) A.B.Ota
Director and Special Secretary,
SCSTRTI

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CHEMISTRY

LESSON PLAN – 2018-19

(1st Year /Class XI)

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Unit - I

SOME BASIC CONCEPT OF CHEMISTRY

L-1 (a) Definition of chemistry, its importance and its branches.

Definition : Chemistry is a branch of science which deals with the composition of matter and the internal changes taking place in it.

Importance : The branch of chemistry finds a lot of applications in our daily life like in (i) Agriculture (ii) Health (Medicine) (iii) Food (iv) shelter (v) Transportation (vi) Computer world (vii) Warfare etc.

Branches : (i) Physical Chemistry
(ii) Inorganic Chemistry
(iii) Organic Chemistry
(iv) Analytical Chemistry
(v) Polymer Chemistry

(b) Definition of matter, elements, Compounds, mixture, afomus and molecules.

Defininion of matter : Matter is any thing which has mass and occupies some space. They are of (i) solids (ii) liquids (iii) Gases (iv) Plasma (v) Bose-Einstein condensation (vi) Fermis - Dirac state.

Elements : The simplest form of a substance which can not further subdivided in any other simple substances. Ex- Iron, Oxygen etc.

Compounds : Two more elements contained in fixed ratio by mass, lose their identies and can be decomposed info its constituent elements by suitable chemical methods. Ex : H_2O, CO_2 etc.

Mixture : It is a combination of two or more elements or compounds in any proportion and retain their identies and can be separated easily by physical process. Ex- salt solution, mixture of sand and salt etc.

Atom : The simplest form of an element which may or may nor exist freely and take part in chemical combination.

Molecule : The simplest form of a compared which exist freely and it is composed of like or unlike atoms. Ex. H_2, CO_2 etc.

L -2 **(a) Law of conservation of mass.**

" During a chemical change, the total mass ofthe product is equal to the total mass of the reactants" Example :

$2Na + 2H_2O = 2NaOH + H_2$

From the above reaction, when 46 g of Na reacts with 36 g of H_2O, the weight of NaOH produced in 80 g and the wt of hydrogen produced in 2g.

Reactant	**Product**
46 + 36 = 82	80 + 2 = 82

* A balanced chemical reaction in written is order of satisfy the law of conservation of mass.

(b) Law of constant composition or definite proportion :

"A pure chemical compound always consists same of elements in definite proportion by weight irrespective of its methods of preparation".

Example : Water can be obtained from different sources or can be prepared in the laboratory by heating hydrogen and oxygen, but in all cases the ratio of hydrogen and oxygen by weight is 2 : 16 or 1 : 8.

(c) Law of multiple proportion.

" When two elements combine to form more than one compound, then the masses of one of the elements which combine with a fixed mass of the other element are in a simple whole number ratio".

Example : carbon can combine with the oxygen to form CO and CO_2.

In CO, C : O = 12 : 16 and

in CO_2, C : O = 12 : 32

$\therefore$ Keeping the weight carbon fixed, if we compare the weight of oxygen in the two compounds, it will be 16 : 32 or 1 : 2 which is a simple ratio.

(d) Law of Reciprocal proportions or law of equivalent proportions :

" When two different elements combine separately with a fixed mass of a third element, the ratio in which they do so will be the same or some multiple of the ratio in which they combine with the third element".

Example :

(i) Hydrogen combine with carbon to form methane where C : H = 12 : 4

(ii) Oxygen combines with carbon to form CO_2, where C : O = 12 : 32

$\therefore$ Keeping the weight carbon fixed, when hydrogen and oxygen will combine, they will either combine in previous ratio i.e., 4 : 32 or 1 : 8 or some multiple of it.

In H_2O, H : O = 2 : 16 or 1 : 18 (same ratio)

& in H_2O_2, H : O = 2 : 32 or 1 : 16 which is a multiple of 1 : 8. $\left(\frac{1:16}{1:8}=1:2\right)$

L - 3 (a) Gay Lusac's law of gaseous volume.

According to gay Lusac, " whenever gases combine, they do so in simple ratio of their volume provided all these volumes are measured under similar conditions of temperature and pressure and if the product is a gas, it also bears a simple ratio with the reactant".

Example :

$$2H_2(g)+O_2(g)\longrightarrow 2H_2O(l)$$

$\therefore$ H : O = 2 : 1 (volume ratio) i.e., 2ml of hydrogen can combine with 1ml of oxygen under similar conditions of temperature and pressure.

$$N_{2(g)}+3H_{2(g)}\rightleftharpoons 2NH_{3(g)}$$

Similarly when nitrogen combines with hydrogen to form ammonia, 1 ml of N_2 will combine with 3 ml of H_2 to form 2 ml of NH_3 provided all these volumes are measured under similar condition of temperature and pressure.

(b) Avogadro's law.

" Under similar conditions of temperature and pressure, equal volume of all gases contain equal number of molecules.

Examples :

If 10 CC of hydrogen at room temperatue & pressure contain 'n' molecules of hydrogen, then 10 CC of oxygen at room temperature and pressure will also contain 'n' molecules of oxygen.

Application :

(i) Atomicity of elementary gases.

(i) Molecular wt = $2 \times \text{V.D.}$.

(iii) Molar volume is 22.4 l at NTP

(c) Dalton's Atomic Theory : (1808)

(i) Matter is composed of small, tiny and discrete particles called atoms. Atom can not be created, can not be subdivided

(ii) Atom of the same element are same in mass and properties.

(iii) A forms of the different elements are different in mass and properties.

(iv) Whenever elements combine, they do so in simple ratio of their atoms.

(v) Weight of compound atom (now called molecule) is sum of the weight of constituent atoms.

L - 4: (a) Atomic mass

" The atomic mass of an element is defined as the average relative mass of an atom of an element as compared to the mass of an atoms of carbon (^{12}C) taken as 12.

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

The unit of relative masses of atoms is called atomic mass unit scale and is abbreviated as amu. However, the new symbol used in 'u' (known as unified mass) in place of a.m.u.

1 a.m.u = 1.66056×10^{-24} g

Mass an atom of hydrogen = $1.6736 \times 10^{-24}\,\text{g}$.

Thus, in terms of amu, the mass of hydrogen atom =

$$\frac{1.6736 \times 10^{-24}\,\text{g}}{1.6605 \times 10^{-24}\,\text{g}} = 1.008\,\text{amu}$$

Molecular mass :

Molecular mass of a substance may be defined as the average relative mass of the molecule as compared (^{12}C) taken as 12".

The molecular mass may be calculated as the sum of the atomic masses of the atoms present in a molecule. For example molecular mass of the CH_4

= Atomic mass of C + 4 × Atomic mass of H.

= $12.001 + 4 \times 1.00\,8$

= $16.033 \approx 16 : 0$.

Molar Mass :

Mass of 1 mole of a substance is called molar mass. It is same as that of molecular mass.

L-5 & 6 : Mole concept (I & II)

It should not be confused that the word "MOLE" is an abbreviation for the word "MOLECULE".

1 Mole $\neq$ 1 Molecule

To start with, 1 mole represents three things (i) wt (ii) volume (iii) Number.

1 Mole $\longrightarrow$ 1. gmol. wt.

1 Mole $\longrightarrow$ vol (gas) $\longrightarrow$ 22.4 *l* at NTP

1 Mole $\longrightarrow$ Number $\longrightarrow$ Avogadro's number of molecule.

A. Weight

1g Mol.wt $\neq$ 1 g

1 g mol.wt means, molecular weight expressed in gram multiplies by 1 (one).

Example : (Compound)

1. Mol. wt of CO_2 = 44

$\therefore$ g mol.wt of CO_2 = 44 g

$\therefore$ 1g Mol. wt of $CO_2 = 1 \times 44g = 44$ g

$\therefore$ 44 g of CO_2 = 1 Mole of CO_2

or, Mole of CO_2 will weigh 44g

Mol. wt of $Na_2\ CO_3$ = 106

1 g Mol.wt of Na_2CO_3 = $106\,g \times 1 = 106\,g$

$\therefore$ 106 g of Na_2CO_3 = 1 mole of Na_2CO_3

or 1 Mole of Na_2CO_3 will weigh 106 g

Elements :

Almost all elements exist in monoatomic state for which atomic weight of the element in equal to its molecular weight, except.

(i) Diatomic elements : H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2.

(iii) Triatomic elements : O_3 (ozone)

(iv) Tetra atomic elements : P_4

(v) Octa - atomic Elements : S_8, Se_8

For multiatomic elements, molecular weight of an element is not equal to its atomic weight.

Example :

Mol. wt of Nitrogen (N_2) = $14 \times 2 = 28$

$\therefore$ 1g Mol. wt of nitrogen = $1 \times 28g = 28g$

$\therefore$ 28 g of nitrogen = 1 mole of nitrogen

or 1 mole of nitrogen will weigh 28 g

B. Volume

1 Mole of any gas occupies colume of 22.4 l at N.T.P.

$\therefore$ 1 Mole of CO_2 = 22.4 l at NTP = 44 g

Similarly, 1 Mole of N_2 = 22.4 l at NTP = 28 g

C. Number

1 Mole of any substance contain Avogadro's number of molecules.

Avogadro's number :

The number of atoms present in 12g of ^{12}C is known as Avogadro's number. In order to determine this number precisely, the mass of one carbon-12 atom was determined by a mass spectrometer and was found to 1.992648×10^{-23} g . knowing 1 mole of carbon weighs 12g (since carbon exist in mono atomic state), the number of atom in it is equal to :

$$\frac{12\text{g}/\text{Mol } ^{12}\text{C}}{1.992648 \times 10^{-23}\text{g}/ ^{12}\text{C atom}}$$

$$= \quad 6.0221367 \times 10^{23} \text{ atoms / Mole}$$

$$\approx \quad 6.022 \times 10^{23} \text{ atoms}$$

This number is called Avogadro's number or Avogadro's constant and symbolined as N_A.

$\therefore$ A Mole of CO_2 = 44g = 22.4 l at NTP.

= 6.022×10^{23} molecules

D. Atoms (Compounds)

Once we are able to calculate the molecules of a compound it is possible to calculate atoms present in it. The formula represents 1 molecule of a compound.

$$\begin{tikzcd}
 & \text{wt (1g mol. wt)} \arrow[d] & \\
1\text{Mole} \arrow[r] & \boxed{6.022 \times 10^{23} \text{ molecule}} \arrow[d] & 22.4\ell \text{ of a gas at NTP.+} \arrow[l] \\
 & \boxed{\text{ATOMS}} &
\end{tikzcd}$$

Example:

1 Molecule of H_2SO_4 contain 7 atoms or 1 Molecule of H_2SO_4 contain 4 oxygen atoms.

Elements :

1, g, at.wt contain 6.022×10^{23} atoms.

For example, 1 g atomic weight of Na in 23g and hence 23g of Na contain 6.022×10^{23} atoms of sodium.

(It may be noted that 1 g at wt $\neq$ 1g except for hydrogen)

HOMEASSIGNMENT

Q1. 2 mole of acetic acid weigh ________ g.
Q2. 7 g of nitrogen is __________ mole.
Q3. 35.5 g of chlorine contain _________ number of molecules.
Q4. 6.3 g of nitric acid contain _________ number of atoms.
Q5. _______ g of magnesium contain as much atoms as 20 g of Calcium.
Q6. 62 g of phosphorous contain _________ atom.
Q7. 16 g of oxygen will occupy _______ ml at NTP.
Q8. 3.011×10^{22} atoms of sulphur will weigh _______ g.
Q9. 3 moles of water contain ________ number of oxygen atoms.
Q10. 11.2 ml of CO_2 at NTP contain ______ moles.

L – 7 : Equivalent masses of compounds.

Compounds are of four types : They are : (a) Acids (b) Bases (c) Salts (d) Oxidising and reducing agents.

(a) Equivalent mass of acid = $\dfrac{\text{Molecular mass of acid}}{\text{Basicity of acid}}$

$$= \frac{\text{Molecular mass of acid}}{\text{Number of replaceabe hydrogen atom present in the acid}}$$

Example :

(i) Molecular mass of HCl = 36.5

$\therefore$ Equivalent mass of HCl = $\dfrac{36.5}{1} = 36.5$

(ii) Molecular mass of $H_2SO_4 = 98$

$\therefore$ Equivalent mass of $H_2SO_4 = \dfrac{98}{2} = 49$

(b) Equivalent mass of base = $\dfrac{\text{Molecular mass of the base}}{\text{Acidity of the base}}$

$$= \frac{\text{Molecular mass of the base}}{\text{Number of replacable OH group present in a base or its equivalent}}$$

Example :

(i) Molecular mass of NaOH = 40

$\therefore$ Equivalent mass of NaOH = $\dfrac{40}{1} = 40$.

(ii) Molecular mass of $Ca(OH)_2 = 74$

$\therefore$ Equivalent mass of $Ca(OH)_2 = \dfrac{74}{2} = 37$

(iii) Molecular mass of MgO = 40

$\therefore$ Equivalent mass $= \dfrac{40}{2} = 20$

($\therefore$ one oxide ion is equivalent to two OH ions).

(c) Equivalent mass of salt = $\dfrac{\text{Moleular mass of salt}}{\text{Number of metal} \times \text{its valency}}$

= Equivalent mass of cation + equivalent mass of anion

(Equivalent mass of an ion - $\dfrac{\text{ionic mass}}{\text{valency}}$)

Example :

(i) Molecular mass of $Na_2CO_3 = 106$

$\therefore$ Equivalent mass $= \dfrac{106}{2 \times 1} = \dfrac{106}{2} = 53$

(ii) Molecular mass of $Al_2(CO_3)$ = 234

$$\therefore \quad \text{Equivalent mass} = \frac{234}{2\times3} = \frac{234}{6} = 39$$

= Equivalent mass of Al^{3+} + equivalent mass of CO_3^{2-}

$$= \frac{27}{3} + \frac{60}{2} = 39$$

(Equivalent mass of an ion - $\frac{\text{ionic mass}}{\text{valency}}$)

(d) Equivalent mass of oxidising and reducing agent

$$= \frac{\text{Molecular mass}}{\text{change in oxidation number}}$$

Example :

(i) $KMnO_4 \longrightarrow MnSO_4$

(O. N. of Mn changes from +7 to +2)

Molecular mass of $KMnO_4$ = 158

$$\therefore \quad \text{Equivalent mass} = \frac{158}{5} = 31.6$$

L- 8 (a) Percentage Composition:

In order to determine the molecular formula of a compaind, it is necessary to know the percentage of each elements present in the compound known as mass percentage composition. Mathematically,

Mass percentage of an element

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

Example :

Let us calculate percentage of carbon present in glucose.

Molecular mass of glucose $C_6 H_{12} O_6 = 6\times12 + 1\times12 + 16\times6 = 180$

Mass of carbon = 72

$$\therefore \quad \text{Mass percentage of carbon} = \frac{72}{180}\times100.$$

Empirical Formula :

" The formula which gives the simple whole number ratio of the atoms of various elements present in one molecule of the compound is called empirical formula".

For example, the formula of hydrogen peroxide is H_2O_2 but its empirical formula is HO.

Similarly, the formula of sodium oxalate is $Na_2C_2O_4$. The empirical formula of it is Na CO_2.

Molecular formula :

"The formula which gives the actual number of atoms of various elements present in one molecule of the compound is called molecular formula".

Compound	**Molecular Formula**	**Empirical formula**
Glucose	$C_6H_{12}O_6$	CH_2
Sucrose	$C_{12}H_{22}O_{11}$	$C_{12}H_{22}O_{11}$
Benzene	C_6H_6	CH
Methane	CH_4	CH_4

Relation between Empirical formula and molecular formula:

From the above examples, it is clear that,

molecular formula = $n \times \text{Empirical formula}$

where 'n' is a simple natural number like 1, 2, 3, 4, ...

$$n = \frac{\text{Molecular mass}}{\text{Emprical Formula mass}}$$

Determination Empirical Formula of a compound.

The empirical formula (E.F.) of a compound can be determined from the percentage composition and atomic mass of different elements present in a compound. The various steps used are as follows :

Step-I : Divide the percentage of each element by its atomic mass. This gives the mole of atoms of certain element in the molecule of the compound.

$$\text{Moles of atoms} = \frac{\text{Percentage of an element}}{\text{Atomic mass of the element}}$$

Step - II : Divide the result obtained in the above step by the smallest value among them to get the simplest ratio of various atoms.

Step - III : Make the values obtained above to the nearest whole number and multiply, if necessary, by a suitable integer to make the value whole number. This gives the simplest whole number ratio.

Step - IV : Wtite the symbols of the various elements side by side and insert the numerical value at the right hand lower corner of each symbol. The formula thus obtained represents the empirical formula of the compound.

Steps for determining of the molecular formula of the compound.

Step - I Determine the empirical formula of the compound as described above.

Step - II Calculate E.F. mass by adding the atomic mass of the atoms in the E.F.

Step - III Determine the molecular mass of the compound. (Either given as such or 2 × vapour density = Molecular mass)

Step - IV Determine the value of 'n' as $n = \frac{\text{Molecular mass}}{\text{E. F. mass}}$

Change 'n' to the nearest whole number if not originally.

Step-V Multiply E.F. by 'n' to get the molecular formula.

(Molecular Formula = $n \times \text{Emprical formula}$) .

Example : An organic compound on analysis gave the following percentage composition:

$C = 57.8\%$, $H = 3.6\ \%$ and rest is oxygen.

The vapour density of the compound in 83, find the molecular formula of the compound.

Solution :

A. Calculation of E.F.

Elements	Percentage composition	At. mass	Mole of atoms	Mole ratio	Simple whole no ratio
C	57.8	12	$\frac{57.8}{12} = 4.82$	$\frac{4.82}{2.41} = 2$	4
H	3.6	1	$\frac{3.6}{1} = 3.6$	$\frac{3.6}{2.4} = 1.49$	3
O	$100 - (57.8 + 3.6)$ $= 38.6$	16	$\frac{38.6}{16} = 2.41$	$\frac{2.41}{2.41} = 1$	2

E.F. = $C_4\,H_3\,O_2$

B. Calculation of Molecular Formula.

E.F. mass = $4 \times 12 + 3 \times 1 + 2 \times 16 = 83$

Molecular mass = $2 \times \text{V.D.} = 2 \times 83 = 166$

$$\therefore \quad n = \frac{\text{Molecular mass}}{\text{E.F. Mass}} = \frac{166}{83} = 2$$

$\therefore$ Molecular formula = $\left(C_4H_3O_2\right) \times 2 = C_8H_6O_4$.

L-9, 10 : Stoichiometry or Problem based on chemical Equation.

Solving of stoichiometric problem is very important. It requires the knowledge of balancing of chemical equation, conversion of units and application of mole concept. The problems are based upon :

(a) Mole to mole relationship

(b) Mass to mass relationship

(c) Mass to Volume relationship

(d) Volume to volume relationship

The main steps in solving such problems are :

(i) Write down the balanced chemical equation.

(ii) Write down the mole or gram atomic or gram molecular masses of the substances whose quantities are given or have to be calculated. In case, there are two or more atoms or molecules of a substance, multiply the mole or gram atomic mass or gram molecular mass by the number of atoms or molecules.

(iii) Write down the actual quantities of the substances given. For the substances whose weights / volume have to be calculated, write the sign inter rogation(?)

(iv) Calculate the result by unitary method.

(a) Mole -mole relationship :

Q. How many moles of nitrogen are needed to produce 8.2 moles of ammonia by the reaction with hydrogen ?

Solution : The balanced chemical equation for the synthesis of ammonia is;

$$N_2 + 3H_2 = 2NH_3$$

? 8.2 moles

2 moles of NH_3 are produced from 1 mole of N_2

8.2 moles of NH_3 are produced from $\frac{1}{2} \times 8.2 = 4.1$ moles of N_2.

(b) Mass - mass relationship:

Q. Calculate the amount of water in gram produced by combunation of 16 g of methane.

Solution : The balanced chemical equation for the combustion of methane is ;

$CH_2 + 2O_2 = 2CO_2 + 2H_2O$

16 g 36 g

From the above equation, it is clear that 16 g of CH_4 can produce 36 g of H_2O.

(c) Mass - volume relationship.

Q. Calculate the amount of $KClO_3$ needed to supply sufficient oxygen for burning 11.2 l of CO gas at NTP completely.

Solution :

(i) The balanced chemical equation when CO reacts with O_2 is,

$2\ CO + O_2 = 2\ CO_2$

$\therefore$ $2 \times 22.4\ell$ of CO at NTP requires 22.4ℓ of O_2 at NTP.

$\therefore$ 11.2ℓ of CO at NTP requires = $\frac{22.4}{2 \times 22.4} \times 11.2 = 5.6\ell$ of O_2 at NTP.

(ii) This volume of O_2 is obtained from $KClO_3$

The balanced equation when $KClO_3$ in heated is;

$2\ KClO_3 = 2\ KCl + 3O_2$

$2(39 + 35.5 + 3 \times 16) = 245\,g$ produces $3 \times 22.4\ell$ of O_2 at NTP.

$3 \times 22.4\ell$ of O_2 at NTP is obtained from 245g of $KClO_3$

$\therefore$ 5.6ℓ of O_2 at NTP is obtained from = $\frac{245 \times 5.6}{3 \times 22.4} = 20.416\,g$

(d) Volume - volume relationship

Q. Calculate the volume of O_2 at NTP required to convert 5.2ℓ of CO to CO_2.

Solution : The balanced chemical equation for the conversion CO to CO_2 is :

$2\ CO + O_2 = 2\ CO_2$

$(2 \times 22.4\ell),\ 22.4\ell$

$2 \times 22.4\ell$ of CO requires 22.4ℓ of O_2

$\therefore$ 5.2ℓ of CO requires = $\frac{22.4 \times 5.2}{2 \times 22.4} = 2.6\ell$ of O_2 at NTP

HOMEASSIGNMENT

(a) 5 moles of H_2 react with 3 moles of N_2 calculate the moles of $NH_3(g)$ formed. What is the limiting reagent in it.

(b) 0.84 g of sodium bicarbonate is strongly heated calculate the sodium carbonate formed.

(c) Find the mass of sulfuric acid need to neutralise 0.01 gram equivalent of caustic soda.

(d) 1 gram of KCl(aq) reacts with 1 gram $AgNO_3$(aq). Calculate the mass of AgCl formed.

(e) Calculate the mass of iron which will be converted into Fe_3O_4 by action of 18 gram of steam.

(f) 1.5 g of impure sample of sodium sulfate (aq) was treated with excess of $BaCl_2$ to form 1.74 g of $BaSO_4$ (dry). Calculate the % of purity of the sample.

UNIT - II

STRUCTURE OF ATOM

L-11 (a) Discovery of electrons :

Towards the second half of 19th century, the passage of lectricity through gases was discovered by Crook which led to the discovery of subatomic particles like electrons and protons.

Discharge tube experiment or discovery of cathode rays :

Digram :

When the pressure inside the discharge tube was reduced to 0.06 to 0.03 mm of Hg by operating the vacuum pump and the potential difference between the two electrodes in >20,000 volt, the tube begins to glow and a stream of faint greenish light was seen to travel from cathode to ward anode. These are known as **cathode rays**.

Properties :

1. They move in a straight line.
2. They have kinetic energy and hence made up of material particles.
3. They are negatively charged.

   These negatively charged particles which moves in a straight line was named as electrons by Stoney (Thomson discovered the electrons.)
4. The e/m ratio of cathode ray particles in $1.76\times10^{8}\ \mathrm{C/g}$.
5. The charge of each cathode ray particle is 1.602×10^{-19} C.
6. Irrespective of the nature of the cathode and the gases taken inside the discharge tube, the charge to mass ratio (e/m) values of cathode rays remains constant. Therefore, electrons (which constitute the cathode rays) are the fundamental constituent of all matters.

(Fundamental means which cann't be further subdivided).

(b) Discovery of proton :

In 1886, M=Goldstein experimented with discharge tube having **perforated cathode** and showed the presence of another type of radiation that passes through the holes of the perforated cathode. These rays are known an anode rays (since it moves away from anode) or canal rays.

Properties :

1. These rays move in a straight line.
2. These rays posses kinetic energy and hence posses mass.
3. These rays are positively charged.
4. The e/m ratio of these particles are variable - Why ?

   (Anode rays are not necessarily protons. These are positively charged residue left after the removal of one or more electrons) and since the charge over the anode ray particles are variable, therefore, e/m ratio values also variable.)

   Anode rays becomes proton when the discharge tube in filled with hydrogen gas. (Hydrogen atom has only are electron and are proton. : $H – e^- = H^+$, proton).
5. The charge of proton = 1.602×10^{-19} C

   The mass of proton = 1.67×10^{-24} g

(c) Discovery of neutron

(The phenomenon of radio activity was discovery in 1896 by Henry Becquerel).

In 1932, James Chadwick, bombarded α -particles on berylium metal and observed that a stream of highly penetrating rays were produced. These rays are neutral in nature and are called neutrons.

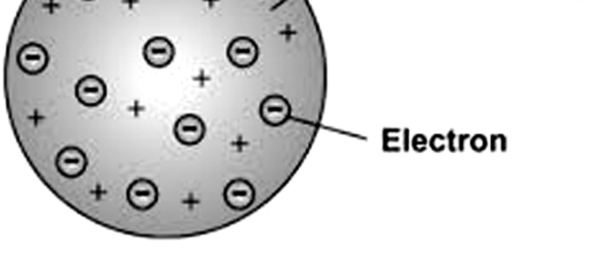
$$ {}^{4}_{2}\text{He} + {}^{9}_{4}\text{Be} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}\text{n} \rightarrow \text{ neutrons.} $$

Mass of Neutron = 1.675×10^{-24} g

L-12 & 13

(a) Thomson's atomic model :

In 1898, Thomson suggested an model for an atom. According to him, "model is a positively charged sphere made up of protons in which electrons are **embeded** whose number is equal to the number of protons."



(b) Rutherford's model :

Introduction :

In order to verify the validity of the Thomson's atomic model, sir Rutherford carried out an experiment in 1911 which led to the discovery of nucleus and he suggested a model for an atom which is named after his name.

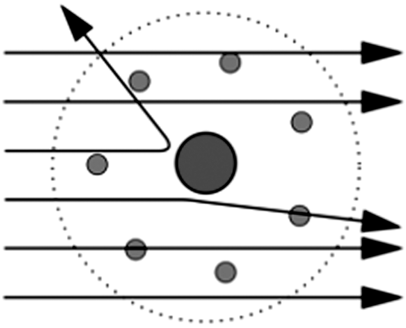
Experiment :

He took three apparatus for his experiment.

(i) a source of α - rays.

(ii) a thin gold foil (~ 100 nm thickness)

(iii) a screen coated with ZnS.



The α -rays are allowed to strike the gold foil. The α -rays which are capable of penetrating the gold foil will strike the screen coated with ZnS kept behind it and produces scintillation (tiny glow.)

He took a very small portion of the gold foil and enlarged it thousand times and observed the followings.

Observation

1. A large number of α -rays are capable of passing freely through an atom (Thin gold foil).
2. One or two of the α -rays out of some thousands of α -rays rebounded back or retraces its own path centrally.
3. Some of the α -rays are deflected from its own path with small angles.

Conclusion

1. Atom consists of a large amount of vaccant space.
2. A positively charged particle in placed centrally inside the atom and it occupies very small space which is responsible for refulsion of α -rays which are positively charged.
3. The deflection of α -rays is due to repulsion from the centrally placed +vely charged particle.

Discussion :

From the Rutherford's experiment, it is clear that the atom posses two parts :

(a) The nucleus (+vely charged)

The nucleus consists of proton (neutron was not discovered at that time) and hence it is positively charged and is capable of repelling the α -particles (which are +vely charged) and it occupies very very small portion of entire atom.

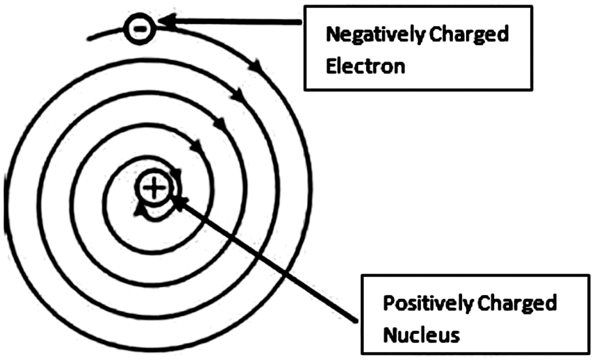
(b) **The extra nucleus** consists of electrons.

If the electron remains in **static** condition out side the nucleus, the electrostatic force of attraction of nucleus will force the electron to fall with it by which the nucleus becomes **neutral.** Once nucleus becomes neutral, it will lose its capacity to repell α -rays.

In order to overcome the above draw back Rutherford suggested that the electrons are revolving around the nucleus in circular path by which the centrifugal force possessed by the movingt electron will balance the electrostatic force of attraction of the nucleus.

Draw backs

1. "According to the theory of electro-dynamics, when a charged particle moves around another charged particle, the moving charged particle will continuously emit energy".



This is applicable in Rutherford's atomic model. Electron, a charged particle in moving around the nucleus which is also a charged particle, will continuously emit energy and ultimately will fuse with the nucleus by which the nucleus becomes neutral, once, the nucleus becomes neutral, it will loose its capacity to repell α-particles. Therefore, either Rutherford's observation is wrong or the theory of electro-dynamics is wrong.

2. Suppose, electron loses energy continuously, then the spectra would have been a continuous spectra instead of a discontinuous spectra.

L - 14 and 15

(a) **Atomic number (Z)**

Atom is electrically neutral and hence number of proton must be equal to number of electrons and this number is called atomic number. It is written as subscript in the left sidebottom of the symbol of an element.

$$\boxed{Z = p = e^-}$$

(b) **Mass number (A)**

Mass number is the sum of number of proton and number of neutrons and it is symbolised as 'A' and written as superscript in the left side top of the symbol of an element.

$$\boxed{A = p + n}$$

If ‘X’ is the name of the element, then it is representer as :

$^{A}_{Z}X$; indicating atomic number and mass number.

$\boxed{n = A - Z}$

(c) Isotopes :

“Elements having same atmic number but different mass number are related to each other as isotopes”.

Examples :

$\mathbf{^{1}_{1}H}$	$\mathbf{^{2}_{1}D}$	$\mathbf{^{3}_{1}T}$
Drotium	Deuterium	Tritium
$e^{-} = 1$	$e^{-} = 1$	$e^{-} = 1$
$p = 1$	$p = 1$	$p = 1$
$n = 0$	$n = 1$	$n = 2$

isotopes of an element varies in their mass number due to variation in the number of neutrons.

Importance :

The fractionalk atomic mass is due to the presence of isotopes. For example, $^{35}_{17}Cl$ and $^{37}_{17}Cl$ are two isotopes of chlorine always exist in 3:1 ratio. The refone, the average atomic mass of chlorine is :

$$\frac{35\times3\times37\times1}{4} = 35.5$$

(d) Isobers :

“Elements having same atomic mass but different atomic number are related to each other an isobers”.

Examples : $^{14}_{6}C$ and $^{14}_{7}N$ are pair of isobers. and $^{40}_{18}Ar$ and $^{40}_{20}Ca$ are also pair of isobers.

(e) Isotomes :

“ Different elements having same number of neutrous are related to each other as isotones”.

For example : $^{16}_{8}O$ and $^{14}_{6}C$ are isotones of each other since both of them posses 8 neutrons each.

$$\left({}_{8}O^{16} \longrightarrow n = 16 - 8 = 8\right)$$

$${}_{6}C^{14} \longrightarrow n = 14 - 6 = 8$$

Similarly $^{76}_{32}Ge$ and $^{77}_{33}As$ are isotones of each other.

(f) Isoelectrons “

“Neutral atom or ions of different elements having same number of electrons are called isoelectronic species”.

For example, $^{20}_{10}Ne$, Na^{+} .Mg^{2+}, $A\ell^{3+}$, N^{3-}, O^{2-}, F^{-} posses 10 electrons each similarly

$^{40}_{18}Ar$, K^{+}, Ca^{2+}, Cl^{-} etc possess 18 electrons each.

L - 16

(a) Spectra :

A spectra is an arrangement of waves as particles which are spread out according to the increasing or decreasing order of wavelength or frequency.

Types

Depending on the nature of source, there are two types of spectra.

A. Emission spectra

B. Absorption spectra

Emission spectra :

Emission spectra can be obtained from the substances which emit radiation on excitation. The excitation can be done as :

(i) by heating a substance in a flame at high temperature (Flame test).

(ii) by passing electric current through thin filament of high melting point metals like W, Mo etc.

(iii) by passing electric discharge through a gas at low pressure (Discharge tube expt.).

Emission spectra are of two types :

(1) Continuous spectra (2) Discontinuous spectra.

Continuous spectra :

When a ray of light passes through a prism, it breaks in to seven clours, VIDGYOR, known as a visible spectra,

(Violet, $\lambda = 4000\overset{0}{A}$, Red, $\lambda = 7000\overset{0}{A}$) $\left(1\overset{0}{A} = 10^{-10}\text{cm}\right)$

Discontinuous spectra are of two types

(i) Band spectra and (ii) Line spectra

Band spectra (Molecular spectra)

The band spectra consists of a number of bright bands separated by dark spaces. Each band is sharp at one end and gradually fades towards the other end. It is exhibited by molecules.

Line specta (Atomic spectra).

When an electron of an atom excited. It jumps from lower energy level to higher energy level and when it jumps back from higher energy level to lower energy level, it emits energy which appears in the form of lines known as line spectra. It is characteristics of an atom. (The spectra of hydrogen atom is explained separately).

Absorption spectra :

If a ray of light is allowed to pass through NaCl solution and then allowed to pass through a prism, there will be an absence as dark space in the yellow region of visible spectra. This type of spectra is known as absorption spectra (Energy is being absorbed corresponding to certain wave length).

(b) Plank's Quantum Theory of Radiation

(Quantisation of energy)

In 1900, Max plank, a German physicist, studied the spectra lines obtained from thermal radiations emitted by hot body (black body) at different temperature and gave the following postulates.

(Quantum is a latin word which means "how much".)

(1) A hot body emits radiations not continuously that is not as continuous wave as suggested by classical Maxwell's wave theory but as discontinuously.
(In case of light, quantum in known as photons. Photon is considered to be massless bundles of energy)

(2) $E \propto \nu$ or $E = h\nu$ .... (i)

E = energy associated with each quantum.
r = frequency of emitted radiation or light

6.624×10^{-34} J.sec.

where 'h' is called Plank's constant and its value is 6.624×10

$$\because \quad \nu = \frac{c}{\lambda}; \qquad \therefore \quad E = \frac{hc}{\lambda} \text{ .... (ii)}$$

Where c is the velocity of radiation and λ is wave length of radiation.

3. The energy emitted or absorbed by a body can be either equal to one quantum of energy or any multiple of natural number.

$$\therefore \quad E = nh\nu$$

where n = 1, 2, 3 .... and can not be fraction.

L-17 : Bohr's atomic model

Introduction : In order to overcome the drawnbacks of Rutherford's atomic model and to explain the origin of the atomic spectra Neil Bohr in 1913 gave the following postulates for an atom.

1. The electrons are moving around the nucleus in circular paths having definite radii.
2. The electrons move around the nucleus in stationary orbits without losing-energy because energy in fraction of a quantum can not be lost (according to Plank's quantum theory).
3. Electrons can occupy any one such paths but it will occupy such a path for which its angular momentum is an integral multiple of $h/2\pi$; i..e,

   Angular momentum, $mvr = n\dfrac{h}{2\pi}$

   Where n = 1, 2, 3 .... etc.
4. Radius the path for 'H' like atom is, $r = \dfrac{n^2h^2}{4\pi^2me^2}$
5. Energy of the path for 'H' like atom is $E = \dfrac{-2\pi^2 me^4}{n^2h^2}$
6. Electrons can jump from one energy ;evel to another which accounts for the origin of the spectra.

   $\Delta E = E_2 - E_1$
7. Each orbit possess certain capacity to accomodate electrons. This is given by $2n^2$ rule, where 'n' is the number of path.

Value of n	Name of the path/ shell/orbit	Capacity of the shell
1	K - Shell	$2 \times 1^2 = 2$
2	L - shell	$2 \times 2^2 = 8$ and so an

8. The outer most shell will maximum contain '8' electrons.
9. The penultipate shell will maximum contain 18 electrons.

Draw backs :

1. Bohr's model is only applicable to hydrogen like atm i..e, it could explain the spectral behaviour of only one electron system like H, He^+, Li^{2+} etc.
2. The quantisation of angular momentium is purely arbitary one.
3. It could nor explain "Zeeman's effect", "The splitting of a spectral line in to closely spaced cluster of spectral lines under the influence of an external magnetic field is known as Zeeman's effect".
4. It could nor explain the "Stark effect".

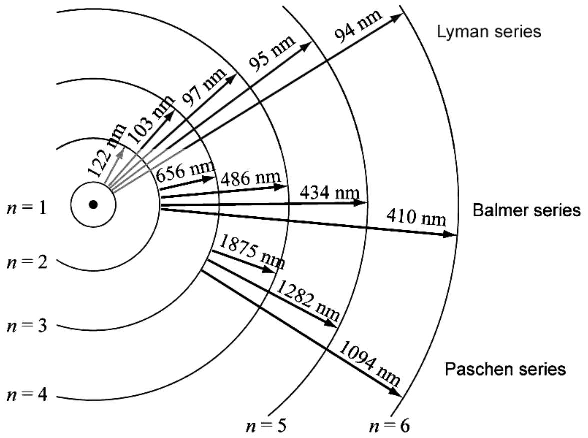
   " The splitting of a single spectral line into closely spaced cluster of spectral lines under the influence of an external field is called Stark effect".

L-18, L-19

(a) Spectra of 'H' like atom :

When electron jumps from higher energy level (n_2) to lower energy level (n_1), it emits energy and the spectra so obtained in known as emission spectra. The emission spectra for 'H' like atom (one electron system is as follows)

Name of the series	**n_1**	**n_2**	**Region**
Lyman series	1	2, 3, 4.....	U.V
Balmer series	2	3, 4, 5.....	visible
Paschen series	3	4, 5, 6.....	Near IR
Bracket series	4	5, 6, 7.....	I. R.
P fund series	5	6, 7.........	Far I.R.



(b) de Broglie's matter wave :

In 1924, a French physicist, de Broglie, extended the idea of dual nature of light (wave as well as particle in nature) to material particles like electrons, protons, neutrous, atoms & molecules etc. in motion have dual character i.e. both particle as we as waves. The wave associated with material particle in known as "matter wave".

Distinction between matter wave and Electro-magnetic wave.

E.M. wave

(1) In E.M. wave the particle of the medium vibrates in its mean position from which energy in deteched in the form of wave.

(2) The velocity of E.M. wave is constant and it is about 3×10^8 m/sec.

Matter wave

(1) In matter wave, the particle of the medium move along with the wave.

(2) In matter wave the velocity depends upon the velocity of the particle which is variable.

Derivation of wave length of matter wave.

We know that energy of radiation, E, related to its frequency, ν, by Planck's quantum theory as,

$$E = h\nu$$

$$\text{or} \quad E = \frac{hc}{\lambda} \quad \text{............ (1)}$$

Again we know, the energy of radiation, E, is related to mass m, by Einstein mass energy relationship as,

$$E = mC^2 \quad \text{............ (2)}$$

$\therefore$ From equation (1) & (2)

$$\frac{hC}{\lambda} = mc^2 \text{ or } \lambda = \frac{h}{mc} \quad \text{.............. (3)}$$

$$n\lambda = \frac{h}{mv} \quad \text{........... (4)}$$

Where 'v' is the velocity of the particle of mass 'm'.

* It may be noted that de Broglie's matter wave has no significance of macro particles but it has significance only for micro particles like electrons.

** The wave character of electrons was finally experimentally confirmed by two german physicist, Davison and Germer, Who gof **defraction grating** by using a beam of cathode rays (Stream of electrons).

(c) **Heisenberg's uncertainty Principle :**

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

If Δx represents the uncertainty (error) in the measurement of the position and ΔP represents the uncertainty (error) in the measurement of the momentum of a sub atomic particle electron, then according to Heisenberg's uncertainty principles

$$\Delta x.\Delta p \geq \frac{h}{2\pi}.$$

Where 'h' is the Planck's constant.

If, say, the position, is measured accurately, then Δx becomes zero,

$$\text{hence, } \Delta p \simeq \frac{h}{4\pi.\Delta x}$$

$$\simeq \frac{h}{4\pi.0}$$

$$\simeq \text{infinity}$$

Thus, the value of Δp becomes infinite means the measureement of the momentum of the particle can not be made accurately.

(d) **Difference between Orbit and Orbital**

Orbit	**Orbital**
1. It is two dimensional	1. It is three dimensional
2. It is signified by principal Q.N	2. It is signified magnetic Q.N.
3. It indicates the principal shell where electron exist.	3. It indicates the shape of the region where there is maximum probabality of finding the electrons.

L-20 and 21

Quantum Numbers :

Electrons are identical with respect to their charge, mass and other properties. However, the energy content of the electrons differ from each other according to their existance in different shells. Since energy in quantised , we use a set of mathematical numbers to locate an electron and to distinguish between different electrons is known as "Quantum numbers". They are of four types :

1. Principal Quantum number
2. Azimuthal or angular Quantum number
3. Magnetic Quantum number
4. Spin Quantum number

1. Principal Q.N.

It signifies the principal shell where the electron exist. It is symbolised by 'n' and its values 1, 2, 3... etc. So far maximum value of 'n' known is 7, the capacity of each shell is already discussed).

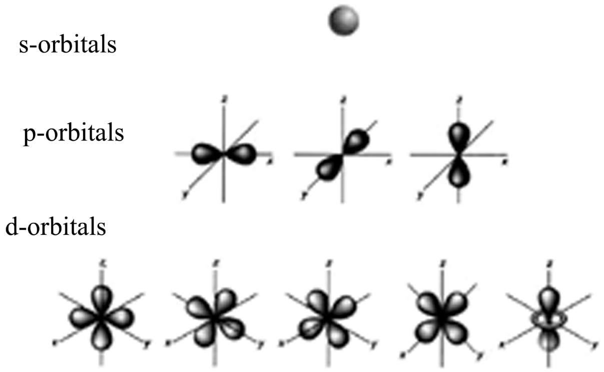
2. Azimuthal or angular Q. N.

It signifies the sub-shell where the electron exist. It is symbolised by '*l*' and its value varies from 'o' to n – 1.

Value of 'n'	**Value of '*l*'**	**Name of the sub-shell**	**Capacity of the sub-shell.**
1	0	s	2
2	0	s	2
	1 '	p	6
3	0,	s	2
	1,	p	6
	2	d	10
4	0,	s	2
	1,	p	6
	2,	d	10
	3	f	14

Maximum number of subshell sofar known is fair and they are s, p, d and f.

Magnetic Q. N.



Magnetic Q.N. signifies the "Shape of theelectrons" which is a misleading term. "It signifies the shape of the region where there is maximum probability of finding electron". These regions are known as orbitals. It is symbolised by 'm' and its value depends upon the value of '*l*'.

m = –*l*, ... 0, ... + *l*

Value of '*l*'	**Valueof 'm'**	**Name of the subshell**	**Shape of the region**
0	0	s	When electron exist in 's' subshell, 'm' has only one value i.e., probability of finding electrons around the nucleous in unidirectional i.e, it is spherically symmetrical around the nucleus.
1.	–1, 0, +1	p	When electron exist in 'p' subshell, 'm' has three values i.e. the probability of finding electrons around the nucleus are in three different directional and they are p_x, p_y and p_z which are dumb-bell shape and are symmetrical around x-axis, y-axis and z-axis respectively.
2	–2, –1, 0, +1, +2	d	When electron exist in 'd' subshell, 'm' have five values i.e., the probability of finding electrons around the nucleus are in five different directions. They are d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$ and d_{z^2}. The shape of d_{xy}, d_{yz} and d_{zx} orbitals are of two dumb-bell shapes. mutually perpendicular to each other and are symmetrical in XY–, YZ and ZX– plane respectively.

			$d_{x^2-y^2}$ orbital is also of two dumb-bell, mutually perpendicular to each other and is symmetrical around X – and Y – axis simultaneously. dz^2 orbital is a dumb-bell shape symmetrical around z–axis and a ring shape in XY–plane.
4	–3, –2, –1, 0, +1, +2, +3	'f'	When electron exist in 'f' subshell 'm' has 7 values i.e., the probability of finding electrons around the nucleus are in seven different directions. However, its shape is not yet known.

4. Spin Q..N.

Electron moves around the nucleus as well as it also moves around its own axis known as spinning. The spinning may be clock wise and or anti clockwise, therefore, spin Q.N. has two values, $+\frac{1}{2}$ and $-\frac{1}{2}$.

($+\frac{1}{2}$ means, out of 2 electrons, are of them has clockwise spin and $-\frac{1}{2}$ means out of two electrons, are of them has anti-clock wise spin.

L-22 and 23

(a) Symbolic representation of an electron when its different Q.N., are given and vice versa.

(i)

Q.N. value	Symbols
n = 1	
l = 0	$1s^1$
m = 0	
$s = +\frac{1}{2}$ or $-\frac{1}{2}$	

(ii)

n = 2	
l = 1	$2p_x^1$ or $2p^1$
m = –1	
$s = +\frac{1}{2}$ or $-\frac{1}{2}$	

(i)

Symbols	Q.N. value
$3d^1$	n = 3 *l* = 2 m = –2/–1/0/+1/+2 $s = +\frac{1}{2}$ or $-\frac{1}{2}$

(ii) $4f^1$

$n = 4$
$l = 3$
$m = -3 / -2 / -1 / 0 / +1 / +2 / +3$

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

(b) Pauli's exclusion principle.

According to Pauli "No two electrons of an atom will have four identical sets of quantum numbers".

Explanation.	**When we write $1s^2$,**
$n = 1$	$n = 1$
$\ell = 0$	$\ell = 0$
$m = 0$	$m = 0$
$s = +\frac{1}{2}$	$s = -\frac{1}{2}$

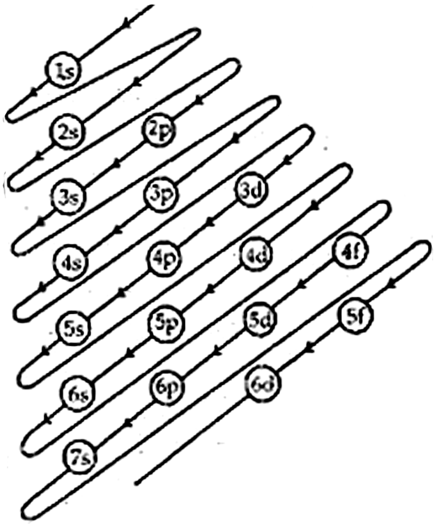
When we represent in box form,

$\boxed{\downarrow\downarrow}$ $\boxed{\uparrow\uparrow}$ or $\boxed{\downarrow\downarrow}$

Correct   incorrect

(c) Auf-bau principle

Auf-bau in a german word which represent the energy level diagram to fill up the electrons i.e., electronise configuration of element. It is as follows :



At - No. (z)	**No of electron**	**Electronic configuration**
1	1	$1s^1$
3	3	$1s^2, 2s^1$
10	10	$1s^2, 2s^2, 2p^6$
19	19	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$
		(Energy of 3d > than that of 4s)
23	23	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^3$
30	30	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$

(The energy of 3d - orbital is greater than that of 4s - orbital because the ‘n+l’ value of 3d - orbital is greater than 4s - orbital.

3d –orbital : $n = 3 ; \ \ell = 2$

$\therefore \ n + \ell = 3 + 2 = 5$

4s - orbital : $n = 4, \ \ell = 0$

$\therefore \ n + \ell = 4 + 0 = 4$)

Exceptional E.C.

“ Based upon the principle that Half-filled or full filled orbitals are most stable, the E.C. of Cu and Cr (Exceptions) are as follows :

Cr –(Z = 24) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$

Cu (z = 29) $\rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$

(d) Hund’s Rule

According to Hund, “the pairing of electrons start only when all the sub-orbitals are being filled or in other words there will be a maximum number of unparity”. For example, when we represent the electronic configuration of nitrogen in boxwise, we have two probabilities, they are :

	1 S	2s	$2p_x$	2py	2pz
N (z = 7)	↑↓	↑↓	↑↓	↑	
	or				
	↑↓	↑↓	↑	↑	↑

The second one is correct according to Hund’s Rule.

Unit - III

CLASSSIFICATION OF MENTS AND PERIODICITY IN PROPERTIES :

L- 24 and 25

Introduction : After discovery of large number of elements, it was necessary to classify then in to blocks having small no of elements so that their properties can be remembered easily. An early attempt was made by classifying all the elements into metals and non metals. It was observed that in each class there are large number of element and more over the position of metalloid and inert gases could not be fixed. Therefore it was decided to classify the elements based on some of its **fundamental** properties and to start with atomic weight was taken to be one of the fundamental properties.

Early History

1. Dobereiner’s triad :

In 1829, J. Dobereiner, a german chemist classified the elements into different groups having three elements in each group based upon the principle that the atomic weight of the middle element is an arithmatic mean of first and third.

Example :

(1)

El	**At. Wt**
Li	7
Na	23
k	39

At wt of Na = $\frac{3+39}{2} = 23$ is exactly the at. wt of Na.

(2)

El	**At. Wt**
Cl	35.5
Br	80
I	127

At wt of Br = $\frac{35.5+127}{2} = 81.25$ is close to the at wt of bromine.

But this method of classification could not be applied to all the elements known at that time and hence discarded.

2. Newland’s law of octave ;

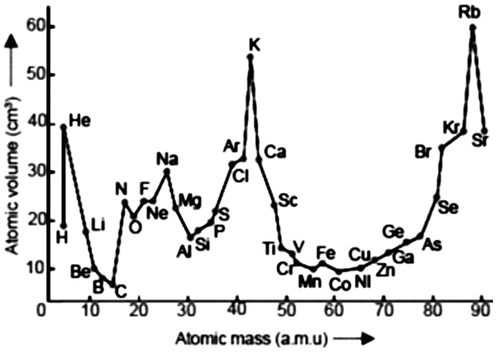
According to Newland (a British chemist, 1863), whenever elements are arranged in the increasing order of their atomic weight, the properties of the eightth element is the repeatation of the first. For example.

Li		Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl	
K		Ca					

The properties of Na is same that of Li, and the properties of Mg is same that of Be etc. But Newland’s way of clasification could not classify all the elements known at that time and hence it was discarded.

3. Lother Mayer’s Curve :

In 1869, a german chemist, lother Mayer, plotted a graph between atomic volume with atomic weight and obtained a curve like graph and found that elements occupying similar positions in the curve have like properties.



However, it was not accepted being its complication in nature.

4. Mandeleev’s periodic table

In 1869, a Russian chemist, D, I. mandeleev gave a law known as mandelev’s periodic law which states that” the physical and chemical properties of the elements are periodic function of their atomic weight”. That means whenever elements are being arranged in the increasing order of their atomic weight, the elements having like properties will occupy one vertical column.

All the elements known at that time could be classified in to a simple rectangular table having seven horizontal rows known as periods and eight vertical coloumn known as groups.

Advantages :

1. all the elements known could be classified in to a simple rectangular table.
2. Knowing the properties of one of the elements in a group, the properties of other elements, in that group can be easily guessed.
3. It gave the guidelines for the discovery of new elements. (Taking the help of mandeleev's periodic table, nearly 40 elements could be discovered within a very short period of time, The refore, Mandaleev is known as "Father of the elements").
4. It could modify the defective atomic weight of the some elements like Be (13 : 5 to 9), In Au, Pt etc.

Disadvantages :

1. **Position of hydrogen :**

   Some of the properties of hydrogen has similarities with Gr-1 elements like electropositive character, combination with non-metals etc. and some of its properties has similarities with Gr-17 elements like diatomic state, nature of bond formation etc. The refore, the position of hydrogen could not be fixed by mandeleev.
2. Group VIII is a trial

Fe	CO	Ni
Ru	Rh	Pd
Os	Ir	Pt

3. Lanthanides and Actinides, each having 14 elements are kept at one flace.
4. Elements having unlike properties are also kept at one place . For example, along with Li, Na and K etc. Cu, Ag & Au are kept. (Na react with cold water vigorously but Cu, Ag & Au never react with water).
5. elements having higher atomic weight comes prior to the element having lower atomic weight. For example, Ar^{40} comes before K^{39}.
6. Position of isotopes could not be fixed.

L-26, 27, 28

(a) Modern Periodic Law.

It states that "The physical and chemical properties of the elements are the periodic function of their atomic number".

Based upon the modern periodic law, a larger number of defects of the mandeleev's periodic table could be modified, such as:

1. The position of isotopes could be fixed since modern periodic table is based on atomic number and atomic number of the element is found to be fixed unlike atomic weight which is variable.
2. In the Madeleev's periodic table Ar^{40} was preceeding K^{39}. On the basis of atomic weight it is a defect but on the basis of atomic number it is not a defect since at no of Ar is 18 and that of K is 19.
3. The position of hydrogen is fixed since the atomic number of hydrogen is 1 and it has the one electron in its outer most like Gr-I elements which have one electrons in their outer most shell unlike Gr-VII elements which have seven electrons in their outermost shell. Therefore hydrogen should be kept in Gr I.
4. In order to avoid the presence of unlike element in a particlar group. Gr - I to Gr - VII are subdivided as IA, IB .. VII A, VII B having 14 vertical coloumns.

But gr VIII was a trial and it is also remain as triad and lanthanides and actinides also containing 14 elements remain as such in modern periodic table.

(Modern periodic table some times known as long form of the periodic table since it contain 18 vertical coloumns unlike 8 in mandeleev's periodic table or 9 in modified farm the mandeleev's periodictable).

(b) The modern periodic table is based an atomic number which indirectly indicate the electronic configuration. The electronic configuration is made according to the auf-bau principle.

According to the electronic configuration, the elements are gouped in to four blocks according to the existance of its outermost electron. They are (i) s - Block (ii) p-Block (iii) d-Block and (iv) f-Block elements.

(i) s-Block Elements

The elements which belong to IA(1) and II A(2) groups are called s-Block elements since in these elements their outermost electrons exist in s-subshell. Elements belonging to these groups have ns^{1-2} electronic configuration of their outermost shell.

Properties

1. They a have the common group valency of +1 and +2.
2. They are strong metals and good conductor of heat and electricity.
3. They form ionic compounds.

(ii) p-Block elements.

The elements belonging to Gr-III A(13) IV A(14), VA(15), VI A(16), VII A(17) are called p-Block elements and they have np^{1-5} electronic configuration in their outer most shell. (Elements having np^6 electronic configuration are inert gases except He which has $2s^2$ E.C.).

Properties :

1) Most of these elements are metals. Some of them are metalloids and some of them are weakly metals.
2) Most of them are bad conductor of heat and electricity.
3) They form both covalent and ionic compounds.

(iii) **d-Block elements**

The elements of IB (11), II B (12), III B (3) IV B (4), VB (5) , VI B (7) and Gr-VIII (8, 9, 10) are called d-Block elements. They have $(n-1)d^{1-1-0}$, ns^{0-2} electronic configuration in their two outer most shell. These elements are called transition elements and act as a transition between most electropositive (s-Block) and most electronegative (p-Block) elements.

Properties :

(1) All these elements are metals and hence good conductor of head and electricity.
(2) They are malleable and ductile.
(3) They form coloured compounds which are either ionic or complex salts.
(4) They have variable valencies.

(iv) f-Block elements :

Two sets of elements (each having 14 in number) belonging to 6th period (Lanthanides) and 7 th period (Actinides) of Gr-III B (3) of the periodic table are called f-Block elements. They have $(n-2)f^{1-14}$, $(n-1)d^{0-1}$, ns^2 electronic configuration in their three outermost shell. These elements are called inner transition elements.

Nomenclature of Elements with atomic numbers > 100.

The naming of the new elements had been traditionally the privileage of the discoverer or discoverers. In recent years this has led to some controvercy. In order to avoid such problems, the IUPAC has recommendation that until the discocvery of a new element is proved and the name is officially recognised. A systematic nomenclature be derived directly from the atomic number of the element using the numerical roots (code) for **'O'** and number from 1 to 9. The roots are put together in order of digits which make up the atomic number and "ium" is added at the end.

Digit	Name	Abbreviations
0	nil	n
1	4n	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

L-29, 30, 31

PERIODICITY

'The variation of the properties of the elements in a period (left to right) and in a group (top to bottom) is known as periodicity)".

1. **Valence Electrons :** " The electrons present in the outermost shell of an element is called valence electrons". As we move from left to right in a period the valence electrons increases from 1 to 8 and in a particular group its remain constant.

2. **Valency :** "The combining capacity of an element taking hydrogen as standard one is called valency". The valency of an element depends upon its valence electrons.

V.EI → 1, 2, 3, 4, 5, 6, 7, 8 (In a period)

Valency → 1, 2, 3, 4, 3, 2, 1, 0 (In a period)

Thus valency increases from 1 to 4 and then decreases to zero in a period. In a group, the valency remain constant since the valence electrons remain constant.

3. **Ionisation potential or Ionisation energy :**

" The amount of energy required to remove an electron from the outermost shell of an isolated atom in its gaseous state is known as ionisation energy (I.E.) w ionisation potential (I.P)".

$$\mathrm{m(g)} + \mathrm{Energy} \longrightarrow \mathrm{M}^{+}_{(g)} + \mathrm{e}^{-}$$

$$\downarrow$$

I.E./I.P

(M → An element)

The factors on which I.E. or I.P. depends are :

(i) No of electrons in the outermost shell :

As the number of electrons in the outermost shell increases, the I.P. value also increases. Therefore, in moving in a period from left to right, this value increases.

(ii) **Distance of the outermost shell from the nucleus :**

As the distance of the outer most shell from the nucleus increases, the attractive capacity of the nucleus over the outermost shell decreases and hence I.P. value decreases down a group.

(iii) **Stability of the electronic configuration :**

The half-filled and full filled obitals are most stable.

Q. Why the I.P. value of nitrogen is greater than that of oxygen ?

Ans. The E.C. of nitrogen (Z=7) is $1s^2$, $2s^2$, $2p^3$ which is either half-filled or full filled state and hence most stable but the E.C. of oxygen in (Z-8), $1s^2$, $2s^2$, $2p^4$ which is unstable, Therefore I.P. value of nitrogen is greater than that of oxygen.

4. Electron affinity (E.A) or Electrongain enthalpy.

" The amount of energy released when an electron is added to an isolated atom in its gaseous state is known electron affinity or electron gain enthalpy (E.G.E)".

$$M_{(g)} + e^- \longrightarrow M^-_{(g)} + \underset{\text{E.A.W E.G.E}}{\underset{\downarrow}{\text{Energy}}}$$

$(M \rightarrow \text{an element})$

* More the stability = More in the energy released
= More the value EA/EGE.

Thus an atom will release more energy if after the addition of one electron to its outer most shell becomes more stable.

In a group, this value decreases having exception.

Q.1. Why the E.A. value of nitrogen is almost zero ?

Ans. The E.C. of nitrogen (Z=7) is$1s^2$, $2s^2$, $2p^3$ which is half-filled state and hence most stable. Therefore, adding an electron to the outermost shell of nitrogen, it becomes unstable and hence its E.A. value is almost zero. No tendency to accept $\overline{e}$.

Q.2. Why E.A. value of fluorine is less than chlorine ?

Ans. When an electron is added to the outer most shell of fluorine (Z=9), it adds to there second shell where as it adds to 3rd shell in case of chlorine (Z=17). The size of 3rd shell is greater than 2nd shell. Therefore, there is less electronic repulsion in chlorine in comparision fluorine and E.A. value of chlorne is greater than that of fluorine.

5. Electronegativity :

"The capacity of an element to attract the shared pair of electrons towards itself in a covalent bond is measured as its electronegativity".

It is measured as sthe average of E.A. & I.P.

$$\therefore \qquad \text{E.N} = \frac{\text{I.P.} + \text{E.A}}{2}$$

usually this value increases in a period and decreases in a group.

6. Atomic size :

"The distance from the centre of the nucleous to outermost shell is called the atomic size or atomic radii".

As we proceed from left to right in a particular period, one more electron is added same shell where as the nuclear chrage gradually increases. Therefore the attractive force of the nucleus becomes more and hence the atomic size decreases except the inert gases.Greater is the p/e ratio smaller is the size.

But on descending down in a particular group, the last electron is added to the next higher shell and hence atomic size increases.

(Ionic size : The size of the cation is less than the neutral atom and the size of the anion is greater than that of the neutral atom).

7. Metallic character .

"The capacity (tendency) of an element to lose its outermost electron is the measure of its metallic character".

It is inversely related to its I.E. value.

On moving in a period, the metallic character decreases and non metallic character increases except for inert gases.

On descending down a group, the metallic character increases.

8. Nature of the oxides :

"Metallic oxides are basic and non metallic oxides are acidic in nature". Therefore, on moving in a period, the basic character of the oxide decreases and acidic character increases and it is reverse in a group.

L-32 - 33

CHEMICAL BONDING AND MOLECULAR STRUCTURE

→ Why do atoms combine to form molecules ?

→ What are the forces that bind the atoms together ?

Causes combination of aroms :

(i) Electronic structure - To attain octet / duplet i.e. stable electronic configuration.

(ii) Net attractive forces between atoms :

(a) Attractive forces between ${}^{n}A - {}^{e}B$ and ${}^{n}B - {}^{e}A$

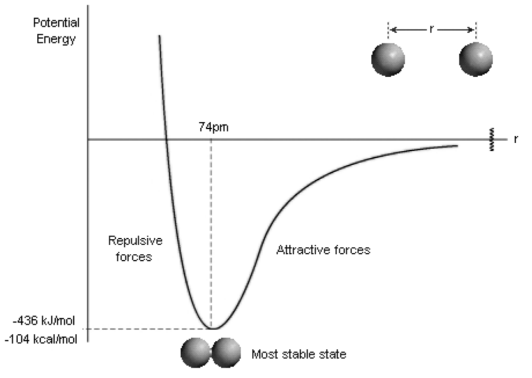
(b) Repulieve forces between ${}^{n}A - {}^{n}B$ & ${}^{e}A - {}^{e}B$

${}^{n}A$ = nucleus of atom 'A' ${}^{e}A$ = electron of atom 'A'

${}^{n}B$ = nucleus of atom 'B' ${}^{e}B$ = electron of atom 'B'

When resulting force is attractive, the two atoms combilne.

(iii) Lowering of energy : At the time of bond formation the energy gets lowered to a minimum internuclear distance. If the distance is reduced further there will be repulaon $\left({}^{n}A - {}^{n}B \text{ and } {}^{e}A - {}^{e}B\right)$ & no-bond formation. The depth of the potential poll is called lowering of energy (or) bond energy & the inter molecular distance of two atoms at which there is maximum decrease of potential energy (PE) is called bond length (r_0). When r_0 is infinity the PE is zero. It decreases where the attractive force anises as the atoms come closer.



(iv) **Octet rule :** Noble gas has the stable configuration with 8 electrons in its valence shall (except He = 2) Thus atoms with less than 8-electron (or 2 - electrons) enter into chemical reaction (bond fdormation) in order to attain stable configuration (Octet or duplet).

Such a stable state can occur by mutual sharing on transfer of one or more electrons.

* **Kossel - Lewis electronic theory of valency.**

(i) Pressure of 2 or 8 electrons in the valence shell constitute the stable structure of atom.

(ii) No. of valence electrons present in outer most orbit of an atom predicts its capacity of an atom to take part in chemical combination / bond formation.

(iii) During bond formation one or more valence electrons either gets transfered or share mutually so that both the atoms attain octet (duplet) configuration. (Noble gas configuration)

(iv) The no. of valence electrons, which an atom loses or gaints or mutually shares to attain noble gas (stable configuration) is called its valency.

(v) The negative and positive ions are stabilised by electrostatic attraction (in case of transference of e-lectron)

* **Ionic or Electrovalent bond :**

Featutes :

(i) This bond occurs between two dissimilar atoms (A & B) of widely very electronegativity value (>1.7).

(ii) Atom ‘A’ has tendency to lose one or more electron(s) to acquire stable electronic configuration by the process of oxidfation

$$A_{(g)} - n\overline{e} \longrightarrow A^{n+}.$$

(iii) Atom ‘B’ (more electro negative element) has tendency to accept one or more electron occupying stable configuration by the process of reduction.

$$B_{(g)} + n\overline{e} \longrightarrow B^{n-}$$

(iv) An electrostatic force of attraction operates between two such oppositely changed ion liberating energy, called lattice energy.

$$A^{n+}_{(g)} + B^{n-}_{(g)} \longrightarrow AB_{(s)} + \text{Lattice energy}$$

Formation of NaCl. (Born - Haber cycle) Refer. Unit VI.

* **Factors affecting ionic bond function**

(i) low ΔiH. Lower is the value easier the cation formation.

(ii) High $\Delta_{eg}H$ $\quad Cl_{(g)} + e^- \longrightarrow Cl^-,\ \Delta_{eg}H = -86.5\ \text{K cal/mol}$

(iii) High lattice energy

$$Na^+{}_{(g)} + Cl^-{}_{(g)} \longrightarrow NaCl_{(s)},\ \Delta H = -182.0\ \text{Kcal/mol}$$

Such force of attraction, $F = \frac{q_1.q_2}{r^2}$

r = inter ionic distance

q_1 = change on cation

q_2 = change on anion

In addition to these, as per Born - Haber Cycle there should be–

(iv) Low heat of submimaation.

e.g. $\text{Na(s)} \longrightarrow \text{Na(vap)} \qquad \Delta H = 26.0\,\text{Kcal}$

(v) Low heat of atomisation or bond dissociation enthalpy.

$$\frac{1}{2}(\text{Cl}-\text{Cl})_{(g)} \longrightarrow (\text{Cl})_{(g)} \quad \Delta H = 28.9 \text{ Kcal}$$

Calculation of $\Delta_{\text{Lattice}}H$

$$\text{Na}_{(g)} + \frac{1}{2}\text{Cl}_{2(g)} \longrightarrow \text{NaCl} \quad \Delta_f H = -94.6 \text{ Kal/mol}$$

As per the cycle –

$$\Delta H_f = \Delta_{\text{sub}}H + \Delta_i H + \frac{1}{2}\Delta_{\text{atom}}H + \Delta_{\text{eg}}H + \Delta_{\text{Lattic}}H$$

$$-94.6 = 26.0 + 119 + 28.9 + (-86.5) + \Delta_{\text{latt.}}H$$

$\therefore \quad \Delta_{\text{latt}}H = -182.0 \text{ K cal/mol}$.

Thus, lattice energy may also can be defined as the energy required by 1 mole of ionic compound (s) to break into constituent ions in gaseous state.

$$\text{NaCl}_{(s)} + 182.0 \text{ K cal} \longrightarrow \text{Na}^+_{(g)} + \text{Cl}^-_{(g)}$$

* **Characteristics of ionic compounds.**

(i) Physical state - hard and rigid

(ii) High density

(iii) High melting and boiling points

(iv) electrical conductivity- Non conductor in solid state but conducts in molten state and in aqueous solution.

(v) Solubility : Ionic compounds are soluble in polar solvents (water) due to ion - solvent interaction liberating energy, $\Delta_{\text{hyd}}.H$. When hydration energy exceeds lattice energy the compound gets soluble in water.

* **Covalent bond** Lewis structure :

Features :

(i) A covalent bond is formed between two similar (B–B) or dis-similar (AB) atoms of comparable electronegativity value i.e., difference of electronegativity (Δ) must be less << 1.7)

(ii) Both the atoms are having short of electron to have octet. They mutually share so that both will have stable configuration.

(iii) If one electron each from A & B share mutually a singlebond(–) is formed i.e., having one shared pair or bond pair.

→ Two electrons simultaneously share forming two bond pairs, a double bond (=) is formed. $:\ddot{\mathrm{O}}::\ddot{\mathrm{O}}:$ i.e. $\mathrm{O=O}$

→ Three electrons form each side (A & B) share having three bond pairs, a triple bond $(\equiv)$ is formed. Here each atom is short of three electrons to have octet having $5\overline{e}_S$ in each of its valence shell.

e.g. $:\mathrm{N}\vdots\vdots\mathrm{N}:$ i.e., $\mathrm{N\equiv N}$

(iv) Covalency of atom is the no. of valence electron that the atom can mutually share with other atom (s) so that both can gave octet / duplet configuration.

e.g. 'N' is trivalent, $:\mathrm{N\equiv N}:$, $-\ddot{\mathrm{N}}=$, $-\underset{|}{\ddot{\mathrm{N}}}-$

It can have a triple bond, on double bond another single bond.or three single bonds.

Example : $(\mathrm{N\equiv N})$, $\mathrm{H-O-N=O}$, $\mathrm{H-\underset{\underset{H}{|}}{N}-H}$

→ Factors affecting covalent bond formation :-

(i) high $\Delta_i H$ (smaller size)

(ii) Equal electron affinity or identical.

(iii) Electro negativity - Comparable electro negativity value.
H-Cl, Cl–Cl, H–H.

→ Distinction between electrovalent bond and covalent bond:

Electrovalent bond :

(i) Formed by transference of electron undergoing redox reactin. One loses e^- & other gains it.

(ii) It is not directional each is an independent sphere (cation / anion) held by electrostatic force of attraction in the crystal lattice.

(iii) Does not form isomerism. Some compound show different geometric arrangement i.e. polymorphic.

(iv) Electrovalent bond is designated as + –. e.g $\mathrm{Na^+\,Cl^-}$

(v) Single charge is equal to $1.6\times10^{-19}\,\mathrm{C}$

Covalent bond :

(i) Formed by mutual sharing as a result both occypy stable configuration (duplet/ octet)

(ii) According to orbital concept the bond is formed by overlapping of atomic orbital is a particular direction. Thus the covalent bon is directional.

(iii) Due to effect arrangement of atoms / bonds is different of atoms / bonds in different direction leads to isomerism.

(iv) Represented by solid stick.
$\mathrm{A-B}$.

(v) Due to polarity, charge on an atom is partial i..e. δ^+ & δ^-.

HOME ASSIGNMENT

(a) Distinguish the characteristics of ionic and covalent compounds.

(b) Provide example in each case

–, = and $\equiv$ bonded molecules.

(c) Explain :

(i) Slubility of carbonates of group-2 decreases from Be to Ba.

(ii) LiCl and NaCl differ in its ionic character.

(iii) NaCl(s) does not conduct electricity ever if it contains Na^+, Cl^- in its lattice.

(iv) Iron shows variable electrovalency.

(v) Carbon is tetravalent while nitrogen trivalent.

(d) Drow the Lewis dot structure of -

H_2S, CO_2, C_2H_4, C_2H_2, C_2H_6.

(e) According to concept of octel classify the following compounds (covalent)

BCl_3, $AlCl_3$, PCl_3, PCl_5, SF_4

L 34, 35

Bond parameters

(i) Bond length : It is the equilibrium distance between the nuclei of two bonded atoms. $H-H$

So covalent radius = $\frac{1}{2}$ (distance between two nuclei of two similar atoms, covalenty bonded.)

$$^{r}A = \frac{^{d}(A-A)}{2}$$

(ii) **Bond order :** (bond multiplicity) No of mutually shared pairs between two atoms of the covalent molecule.

Bond order of O=O is 2

Bond order of $N \equiv N$ is three.

Bond order $\propto \frac{1}{\text{Bond length}}$. $\propto$ Bond strength

(iii) **Bond angle :** Angle between the bonding e^- pairs in a given mlecule or ion.

e.g. < HCH in CH_4 is $109^0\ 28'$

The magnitude of bond angle depends on :

(a) Number of olne pair.

(b) electronegativity and size of central atom & other atoms in a molecule.

(c) Pressence of multiple bond in a molecule.

(iv) **Bond enthalpy :**

$$A + B \longrightarrow AB + \text{ Bond formation energy } (-ve)$$

$$AB \longrightarrow A + B - \text{Bond dissociation energy} (+ve)$$

$H_2 + 435.8\ kJ/mol = 2H_{(g)}\ \Delta_{BE} = +435.8\,kJ$

In case of polyatomic molecules the measureement of bond strength is more complicated, e.g. in H_2O, the enthalpy needed to break the O–H bnd, is not same.

$$H_2O_{(g)} \longrightarrow H_{(g)} + OH_{(g)} \qquad \Delta_a H_1 = 502\ \text{kJ/mol}$$

$$OH_{(g)} \longrightarrow H_{(g)} + O_{(g)} \qquad \Delta_a H_2 = 427\text{kJ/mol}$$

In such case the mean bond enthalpy is used.

$$\text{Mean or average bond enthalpy} = \frac{502+427}{2} = 464.5$$

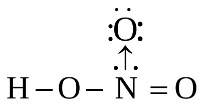
$H_2O_{(g)} + 929(= 2 \times 464.5)\text{kJ} = 2H_{(g)} + O_{(g)}$ O–H bond dissociation energy is not same in ethanol.

Thus is polyatomic the bond dissociation energy depends on chemical environment.

Co-ordinate covalent bond (dative bond) This is a special case of covalent bond where one atom with excess pair of $\overline{e}$ (donor) & other is short of e^- (acceptor).

In stead of – an arrow $(\rightarrow)$ heads towards acceptor. By such both the atoms satisfy stable configuration.

e.g HNO_3



$$H-O-\overset{\overset{\textstyle :\ddot{O}:}{\uparrow}}{N}=O$$

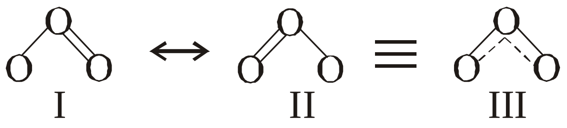
N = donor atom with a pair of e^-.

O = acceptor atom as it has 6 valence electron (short of two $\overline{e}s$).

Here 'N' and 'O' have stable octet configuration

* **Resonance :** According to the concept of resonance whereever a single Lewis structure cann't describe a molecule accurately, a number of structures with similar energy position of nuclei, bonding and non-bonding pairs of electrons are taken as the canoncial structures of the hybrid which describes the molecule (ions) accurately.

Example : $\mathbf{O_3}$



I & II are canonical structures.

III - resonance hybrid

It may be stated that

(i) Resonance stabilizes the molecule

(ii) Resonance averages the bond characteristics as a whole.
e.g. in O_3 all the O–O bonds are identical.

(iii) None of the canonical form can fully describe all the properties of the mlecule or ion.

(v) Greater in the reasonating structure freater in the stability.

Resonance energy = [Energy of its most stable mesomeric form - energy of the structure determined experimentally]

e.g. $$\underset{\text{I}}{O=C=O} \leftrightarrow \underset{\text{II}}{\overset{+}{O}\equiv C-\overset{-}{O}} \leftrightarrow \underset{\text{III}}{\bar{O}-C\equiv\overset{+}{O}} \equiv \underset{\text{IV}}{O\overset{\cdots}{-}C\overset{\cdots}{-}O}$$

I, II and III $\Rightarrow$ canonical omnical forms

IV $\Rightarrow$ resonance hybrid

Resonance energy of CO_2 is 126 kJ/mol, which implies that the energy of CO_2 molecule is less than that of the most stable resonating stricture by an amount of equal to 126 kJ.

Greater is the resonance energy greater is the stability.

* **Valence bond theory** Heitlet and London extended by Pauling and slater.

Features :

(i) Valence shell atomic orbitals of the two atoms over lap to form a covalent bond.

(ii) Orbital with unpair e^- takes part in overlapping and results bond formation. The spin gets paired at this time.

(iii) Maximum electron density is found some where in the overlapped region. The force that binds the atoms in a covalent bond is due to electrostatic attraction between the nuclei and the accumulated electron cloud between them.

(iv) More is the extent overlapping, grater in the strength of the covalent bond. The amount of energy released per mole of **bond-energy**.

(v) Covalent bond is directional i.e. direction of covalent bond is considered to be the region of maximum electron density in the overlapping region.

(vi) It so happens sometimes that paired electrons of the valency shell get unpaired and promoted to vacant orbitals of the same valence shell with slightly higher energy which can only explains the trivalency of B, tetravalency of C, pentavalency of P etc.

Formation of H_2 molecule : Greater extent of overlapping $(\uparrow\downarrow)$ takes place when the inter atomic distance is 74 pm & there is greater lowering of energy indicating net attarctive force between $n_A - e_B$ and $n_B\, e_A$ $(-435.8\,\text{kJ})$.

HOME ASSIGNMENT

Fill in the gaps :

(a) C–O bond in CO_3^{2-} ion is same is due to _______.

(b) The bond order of nitrogen molecule is _______.

(c) Bond angle in water is _______ .

(d) O^+ can form _______ numble of single bonds.

(e) O–O bond length in ozone is shorter/longer than O=O.

L 36, 37, 38

The number of unpair electron that the atom can have in ground or excited state determines the valency of the atom. The orbital with pair of electron does not take part in overlapping process. On the basic of nature of overlapping there occurs two types bond :

(a) σ - bond, overlapping taking place along intermolecular axis (z-axis).

(b) π - bond is formed by lateral overlapping of p-p and d-p orbitals. Due to less extent of overlapping as electron charge cloud, distributes above and below axis (inter molecular axis), it is weaker than $\sigma-\text{bond}$.

→ Between two atoms there exists only one $\sigma-\text{bond}$ because there exists only one inter nuclear axis.

→ About $\sigma-\text{bond}$ free rotation of atoms is possible.

* **Hybridisation :**

It is the process of mixing of-atomic orbitals of an atom of comparable energy providing hybrid (mixed) orbitals of identical shape and energy oriented in space to minimise repulsion among themselves.

→ Steps Enroling hybridisation :

(i) Excition to have required number of unpair electron.

$C^* = 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$

(ii) Mixing and re-orientiation :

e.g. one 's' and two of there p-orbitals mix together to form three sp^2 hybrid orbital directed towards three corners of an equilateral triangle to have angular distance of 120^0 to minimise the electronic repulsion.

→ Conditions of the hybridisation.

→ Characteristic of hybridisation -

→ Types of hybridisation -

(a) sp-hybridisation : s and one 'p' orbitals mix together to form two sp hybrid orbitals directed linearly at an angle of 180'. The % of 's' and 'p' - character is 50%. The two sp. hybrid orbitale are of identical shape but differs from pure s & and p-orbitals. Each hybrid orbital like pure orbital can accomidate two electrons of opposite spin.

e.g. $BeCl_2$ Be $1s^2$

O.N. of Be is +2 i.e. it must hav two unpair electron i.e. it needs excitation.

$^*Be\ \ 1s^1\ \ 2p^1$

Mixing and re-oriention:

Shape of $BeCl_2$ Cl–Be–Cl (linear, bond angle 180^0)

(b) sP² hybridisation : s and two of three 'p' orbitals mix together to form 3 sp^2 hybrid orbitals which directs towards three corners of an equilateral triangle making an angle of 120^0. Each orbitals has 33.3% s-character and 66.6% p-character.

e.g. BCl_3 $\quad {}_5B \quad 1s^2 \quad 2s^2\ 2p^1$

$B \quad 1s^2 \quad \underbrace{2s^1\ 2p_x^1\ p_y^1}_{\text{ThreeSp}^2\text{hybrid orbitals}}$

Bond formation : These sp^2 hybrid orbital (three) overlap axially with p-orbital (with an umpair e^-) of Cl forming three $\sigma-\text{bonds}$.

Shape of BCl_3 : Trigonal, Bond angle - 120^0.

(c) sp³-hybridisation :

s-orbital mixes with all the three p-orbitals (p_x, p_y, p_z) forming four sp^3 (1+3) hybrid orbitals which directs towards four corners of an tetrahetron having an angle of $109^0\ 28'$ minimising the electronic repulsion among themselves.

Examples : CH_4 $_6C$ $1s^2\ 2s^2\ 2p^2$

Excitation C^* $2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$

&

mixing

→ bond formation : The four sp^3 hybrid orbitals overlap with 4 hydrogen (s-orbital) forming $4-\sigma$ bond .

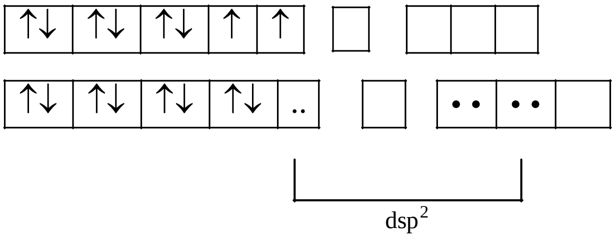
→ Shape of CH_4. tetrahedral, bond angle $109^0\ 28^1$.

(d) dsp^2 **hybridisation** $d_{x^2-y^2}$, s and two of the three p-orbitaly (p_x, p_y) mix together to for 4-dsp^2 hybrid orbitals. These four hybrid orbitals directs towards 4-courses of a square making the angular distance 90^0.

Example :

$\left[Ni(CN)_4\right]^{2-}$ Ni^{2+} $3d^8$ $4s^0$ $4p^0$

Ni^{2+}



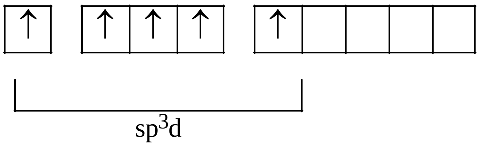
∴ (electron pair of the ligand, CN^-)

(e) sp^{3}d hybridisation :

s, three p-orbitals ad d_{z^2} orbitals mix together to forms five sp^{3}d (1+3+1) orbitals directed towards five corners of a triangular dipyramid making equatorial angle 120^0 and axial angle 90^0. Triangular bipyramid is an unsymmetrical geometry.

$\overset{+5}{P}\ \overset{-5}{Cl_5}$ O.N. tells 'p' must have five unpair electron i.e. in excited state.

* Excition. P^*



* Mixing and re-orientiation :

* Bond formation. The five sp^{3}d hybrid orbitals axially overlap with five Cl-atoms (p-orbital) forming hybrid-pure (sp^{3}d - p) σ - bonds (five)

* Shape : Trigonal bipyramidal

* Bond angles : 120^0 (equatorial), 90^0 (axial)

* Bond length : Axial P-Cl bond > equational P-Cl bond.

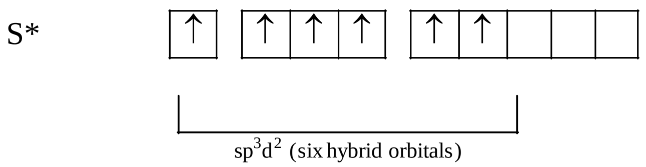
(f) sp^3 d^2 hybridisation : s, three portals and dx^2-y^2 and d_{z^2} mix together to form six sp^3 d^2 hybrid orbitals directing towards six corners of an octahedron making an angular distance of 90^0. This is a symmetrial orientation.

Example :

$\overset{+6}{S}\ \overset{-6}{F_6}$ O.N. predicts, presence of six umpair electrons in the central atom, 'S'.

So excitation step in necessary.

$S = 1s^2\ \ 2s^2\ \ 2p^6\ \ 3s^2\ \ 3p^4\ \ 3d^0$



σ Bond formation : The six sp^3d^2 hybrid orbitals overlap axially with p-orbital of F (having unpair electron) forming six hybrid (sp^3d^2) and pure 'p' orbital forming six σ-bonds.

Shope - Octahedeal. bond angle = 90^0

All S–F bonds are identical.

(g) sp^3 d^3 hybridisation :

mixing of $s+\left(p_x, p_y, p_z\right)+\left(d_{xy}, d_{x^2-y^2}, d_{z^2}\right)=7\ sp^3d^3$ hybrid orbitals.

in which p_x, p_y, $d_{x^2-y^2}$ are in XY plane.

P_z and d_{z^2} are perpendicular to it.

These 7-hybrid orbitals are directed to seven corners of an unsymmetrical pentagonal bipyramid to minimise repulsion. Equational angle = 72^0

Axial angle = 90^0

Example- IF_7

Prediction of hybridisation :

(i) Total no. of valence electrons of the molecule or ion if 8 or less than it the total no. is divided by 2, the division value (quotient), predicts the no. bond pairs.

(ii) If the total no. exceeds more than eight the total number is to be divided by 8. The division value of (quotient) predicts the bond pair & $\frac{\text{reminder}}{2}$ = no. of lone pair.

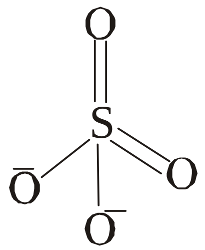
The total no. of stercospecific pairs = no. of bond pairs + no. of lone pairs
= nature of hybridisation.
e.g. 5 (sp^3d), 6(sp^3d^2) etc.

e.g. SO_4^{2-} : No of valence electrons (S=6), 4(O) = $6\times4=(24)$ + 2 (for two negative charges) = 32 electrons

$32\div8=4$ (sp^3) No reminder i.e. having no lone pair.

Thus 'S' undergoes sp^3 hybridisation in SO_4^{2-}

Shape is tetrahedral.



HOME ASSIGNMENT

(a) Distinguish between σ bond and π bond.

(b) Write down the resonating structures of ______

(i) CO_3^{2-} , (ii) benzene, (iii) NO_2 , (iv) N_3^- (azide ion)

(c) In which of the following species $d_\pi - p_\pi$ bonds exist :

SO_3^{2-}, $CO_3^{=}$, PO_4^{3-}, NO_3^-

(d) Predict the nature of hybridisation of carbon in the following compound.

$H - C \equiv C - CH = CH - CH_2 - CH_3$

(e) Draw the orbital overlapping diagram of CH_4, $CH_2 = CH_2$ and $HC \equiv CH$

(f) Fill in the blanks :

(i) The shape of molecule with sp^2 hybridisation is __________ .

(ii) C– undergoes _______ hybridisation in CO_2 .

(iii) Shape of PO_4^{3-} is __________ .

(iv) The lone pair in NH_3 present in ___________ orbital.

(v) BF_3 changes to BF_4^- . So the change of hybridisation is from _______to ______.

L- 39 , 40

→ The covalent bonds are directional as the bonds are formed out of overlapping atomic orbitals. The orbitals have (pure & hybrid) directing lobes in different geometry.

Evidence : (i) Due to directional nature of covalent bonds, the covalent compounds exhibit isomerism.

(ii) Dipolement

VSEPR Theory : Geometry of covalent molecules. Molecule or ion consists two types of electron pairs, bond pair (shared pair), lone pair (unshaved pair). The geometry and shape of the species (molecule/ion) depend on the presence of these pairs as postulated by Nyholon and Gillespie (1957)

Postulates :

(i) Shape of molecule depends on bonded and non-bonded pairs around the central atom.

(ii) Pair of e^- in the valenceshell repel one another since their e^- clouds are negatively charged.

(iii) These pairs of electrons tend to occupy such positions in space that minimise repulsion & thus maximise distance between them.

(iv) The valence shell is taken as sphere with the e^- pairs localising on the spherical surface at maximum distance from one another.

(v) Electron pairs on multiple bond (= or $\equiv$) are single super pair.

(vi) VSEPR model is applicable to only one of the canonical structure in case of resonance.

The electronic repulaion follows in the order : $\ell - \ell$ repulsion > ℓ - b repulsion > b - b repulation.

ℓ = lone pair, b = bond pair.

Lone pair occupied more space in a molceule than bond pair (as it shares between two atoms)

This repulsive effect resulting is deviation of shape and alternating of bond angle. By such molecules can be subdivied as

(a) molecule with only bond pair no lone pair

(b) Central atom of the molecule with one or more lone pairs.

AB_2 , AB_3, AB_4, AB_5 and AB_6 are with only bond pairs.

A = cantral atom, B-bonded atoms, L=lone pair, e.g. $AB_2(BeCl_2)$, $AB_3(BCl_3)$, $AB_4(CH_4)$, $AB_5(PCl_5$, $AB_6(SF_6)$

Shape (geometry) of molecules / ions with different types of hybridisation.

Hybridisation	Molecule type	No of b.p	No of l.p.	Geometry (Arrangement)	Shape	Example
sp^2	(i) AB_3	3	0	Trigonal	Trigonal	BCl_3
	(ii) AB_2L	2	1		Bent	$SnCl_2, SO_2$
sp^3	(i) AB_5	4	0		Tetrahedral	CH_4, N^+H_4
	(ii) AB_3L	3	1	Tetrahedral	pyramidal	NH_3
	(iii) AB_2L_2	2	2		Bent	H_2O
sp^3d	(i) ABr	5	0	Trigonal	Trigonal	
	(ii) AB_4	4	1	bipyramidal	bipyramidal	PCl_5
	(iii) AB_3L_2	3	2		sea saw	SF_4
	(iv) AB_2L_3	2	3		T – shape	ClF_3
					Linear	XeF_2
sp^3d^2	(i) AB_6	6	0	Octahedral	Octahedral	SF_6
	(ii) AB_5L	5	1		square pyramidal	BrF_5
	(iii) AB_4L_2	4	2		Square planar	XeF_4

$\ell - \ell$ repulson compreses the bond angle.

e.g. $CH_4(109^0 28^0)$, : NH_3 (107^0), $\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}H_2$ (105^0).

Polar character of covalent bonds :

Due to difference in electronegativity the shared pair of electron is more shifted towards much electronegative atom when covelentyly bonded.

e.g. $H-CL \longrightarrow \overset{\delta+}{H}-\overset{\delta-}{Cl}$

The less electronegative atom acquires partial positive charge $\left(\delta^+\right)$ while the more electronegative atom acquires partial negative charge $\left(\delta^-\right)$. This unsymmetrical distribution of e^- developes polar character & the molecule is polar. The symmetrical molecules are non-polar, e.g. H_2, Cl_2, F_2, O_2, CH_4, CO_2 etc.

Dipole moment :

Degree of polarity can be quantitatively known from the dipole moment $(\mu) = exd$ i.e. charge × distance and represented as crossed arrow ($+\!\!\!\rightarrow$) pointing towards more electronegative atom.

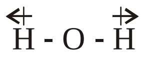
→ Units of μ : charge is order of 10^{-10} esu and distance in the order of 10^{-8}can. So μ in the order of 10^{-18} esu. cm = debye(D). ID = 10^{-18} esu. cm e.g. $\mu_{HCl} = 1.03\,D$

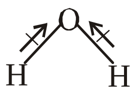
$= 1.03 \times 10^{-18}$ esu. cm. SI unit : 1 esu = $3.325 \times 10^{-10}\,C$, $1\,cm = 10^{-2}\,m$

$\Rightarrow$ ID = 3.335×10^{-30} C m

→ Applications dipolememoment : $\mu(H_2O) = 1.84\,D$

(i) shape of molecules.





Linear $(\mu = 0)$ (BENT)

(ii) Distinction between polar and non-polar molecule -

$\mu = 0$ (non-polar)

(iii) Degree of polarity – $HF(\mu = 1.98\,D) > HCl(1.03\ D)$

So HF is more polar than HCl.

(iv) Calculation of % of ionic-character of covalent bond:

$$= \frac{\text{Experimental } \mu \text{ obs.}}{\text{Theoretical (charg} \times \text{distance)}} \times 100$$

electronic charge = 4.8×10^{-10} esu . = $1.602 \times 10^{-19}\,C$

Covalent character of ionic bond.

Due to polarisation of ions the ionic bond also possess some covalent character e.g. LiCl. It is due to the polarising power of the cation and polarisability (tendency to be polarised or become unsymmetrical) of the anion.Fajan's rule explans the partial covalent character of an ionic bond.

Rule- 1. Higher positive charge of cation.

e.g. Be^{2+} has greater polarissing power than Li^{+}.

2. Smaller size. LiCl is more covalent than NaCl.

$$r_{Li^+} < r_{Na^+}$$

3. Cation with $s^2p^6\,d^{10}$ configuration possesses greater polarising power than with $s^2\,p^6$ configuration

$Z_n^{2+}(2, 8, 3s^2sp^6 3d^{10})$ > Ca^{2+}(2, 8, $3s^2\ 3p^6$)

4. Greater is the negative charge on anino.

O^{2-} gets more polarised F^- i.e. CaO is more covalent than CaF_2.

5. Larger is the size of the anino greater is the tendency to be polarised i.e. higher polarisability.

e.g. LiI is more covalent than LiF.

L-41, 42, 43, 44

Molecular orbital theory (Hund and Mulliken - 1932)

Salient Features

(i) Electrons in a molecules are present in various molecular orbitals as electrons in atom are present in various atomic orbitals.

(ii) Atomic orbitals with comparable energes & proper symmetry combine to form molecular orbitals.

(iii) Electron in an atomic orbital (AO) is influenced by one nucleus but is a molecular orbital (MO) it's influenced by two or more nuclei depending upon the no. of atoms in the molecule i.e. molecular orbital is polycentric.

(iv) The no. of molecular orbital is equal to the number of combining atomic orbitals. When two atomic orbitals combine two MOs are formed : one is bonding (BMO) & other is antibonding mo. (AMO)

(v) The BMO has lower energy than as and AMO.

(vi) Just like atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a mo.

(vii) The e^-(s) are getting filled into the MO(s) obeying aufbau principle, Pauli's exclusion principle and Hund's rule.

Formation MOs (LCAO)

The formation of molecular orbital in the light of wave functions is described by an approximate method known as linear combination of atomic orbitals (LCAO).

For two electron molecular orbitals system (i.e. H_2) may be described by LCAO that can take place by addition and by substraction of wave functions of individual atomic orbitals.

$\psi_{mo} = \psi_A \pm \psi_B$ ψ_A = wave function of atom A

ψ_B = wave function of atom B

Thus, two MOs can be written is

$\sigma = \psi_A + \psi_B$ (Bonding MO) - constructive interference of electron waves (additive)

$\sigma^* = \psi_A - \psi_B$ (AMO) – destructive interference of electron waves.(substractive)

In a bonding molecular orbital $\bar{e}$ density concentrates between the two nuclei while is AMO $\bar{e}$ density is located away from the space between the nuclei. In fact there is a nodal plane between nuclei.

Hence the repulsion between the nuclei is high. Electrons present in BMO tend to hold the nuclei together & fovours bond formation. Electrons in AMO destabilise the molecule. The total energy of two MOS however remains same as that of two original atomic orbitals.

Conditions for the combination of atomic orbitals.

(i) The combining atomic orbitals must have the ssame or nearly the same energy.

(ii) Must have same symmetry about the molecular axis (Z-axis) ($2p_z$ combines with $2p_z$ of other atom but not with $2p_x$ or $2p_y$)

(iii) The combining atomic orbitals must overlap to the maximum extent.

Types of MOs

σ - MOse are symmetrical around the bond axis while π MO_s are not symmetrical. Out of three p-orbitals p_z-p_z forms σ orbitals while p_x–p_x and p_y-y_y form π-orbitals. Thus, $\sigma_{2p_2}, {}^*\sigma_{2p_2}, \pi_{2p_x} - \pi_{2p_y}, \pi^*{}_{2p_x} - \pi^*{}_{2p_y}$ (Three bonding and three antibonding orbitals are formed.)

Energy levels of different molecular orbitals.

→ Upto molecules N_2 ($14e^-s$)

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \left(\pi_{2px} = \pi_{2py}\right) < \sigma_{2p_z} < \left(\pi^*_{2p_x} = {}^*\pi_{2px}\right) < \sigma^*_{2p_z}$$

→ For O_2 and F_2 :

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2pz} < \left(\pi_{2px} = \pi_{2py}\right) < \left(\pi^*_{2p_x} = {}^*\pi_{2p_y}\right) < \sigma^*_{2p_z}$$

Electronic configuration and molecular behaviour :

Nitrogen molecule $\left(14\ \overline{e}\,s\right)$:

$$\sigma_{1s^2}\sigma^*_{1s^2}\sigma_{2s^2}\sigma^*_{2s^2}\pi\,{}_2p_x^2\pi_{2p_y^2}\sigma_{2p_z^2}\ \text{(No unpair electron)}$$

oxygen molecule $\left(16\ \overline{e}\ s\right)$:

$$\sigma_{1s^2}\sigma^*_{1s^2}\sigma_{2s^2}\sigma^*_{2s^2}\sigma^*_{2s^2}\sigma\,{}_2p_z^2\pi_{2p_x^2}\pi_{2p_y^2}\ \pi_{2p_x^1}\pi_{2p_y^1}\quad \text{(Hund's rule obeyed)}$$

→ Stability of molecule :

Greater in the no of electron in bonding MO greater is the stability i.e, bonding influence is more.

→ Bond order :

$$BO = \frac{1}{2}\ (\text{no. of } e^- \text{ s is BMO} - \text{No. of } e^-(\text{s}) \text{ is AMO})$$

A positive or higher is the B0 greater is the stability.

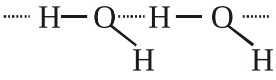
B.O. (N_2) = 3 while B0 (O_2) = 2

→ Bond length : The bond length decreases as bond order increases..

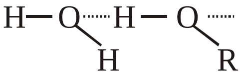
→ Magnetic behaviour : More is the no. of unpair e^-(s) more is the magnetic behaviour i.e. paramagnetic (e.g. O_2 (no of unpair $e^-_s = 2$), paired e^-(s) indicate diamagnetic property (e.g. N_2)

Hydrogen bonding

Definition : Hydrogen bond is an attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O, N) of another molecule of same or different compounds.



(same compound)



(different compound)

It bridges between two covalent bonds.

→ Condition for formation of H-bond

(i) Polar molecule with F, O or N and H

(ii) Electronegative atom must be smaller in size.

→ Types of H-bond :

(i) Inter molecular, (ii) Intramolecular,

(i) Intrermolecular e.g. H–F

(ii) Intramolecular (within the molecule itself)
e.g. O-nitrophenol.

DRAW FIGURE

→ Strength of H-bonding : It is a weaker bond and requires only 5–10 K cal/mol of energy to break. Bond strength is directly related to electronegative value.

$$-H...F- > O-H....O > N-H...N- > Cl-H...Cl$$

Consequence of H-bonding:

Physical properties such as density b.p, m.p viscosity, solubility,molecular spectral lines can be explained on the basis of H-bond.

Example : NH_3 is a covalent compound but soluble in water.
(inter molecular H-bonding)

HOME ASSIGNMENT

(a) Distinguish between (i) atomic orbital and molecular orbital.
(ii) bonding MO and antibonding MO.

(b) Write the electronic configurations of N_2 and O_2.

(c) Explain the following :

(i) Hydrogen is diatomic but He is mono-atomic.

(ii) O_2 is paramagnetic while N_2 is diamagnetic.

(iii) HF is a liquid but HCl a gas.

(iv) Methane is a gas while CH_3OH is liquid.

(v) Glycerol is more viscous than ethylene glycol.

(vi) Water is a liquid but H_2S is a gas.

(vii) Ice floates over water.

(viii) p-nitrophenol has higher m.p. than o-nitrophenol.

(ix) CO_2 is non-polar while SO_2 is polar.

(x) XeF_4 and SF_4 are not of identical shape.

(d) Inter molecular distance of H–F is 0.92^0A. If its dipole moment is 1.98 D. Calculate the % of ionic character of HF.

(e) Find out the magnetic behaviour and bond order in case of O_2^+, O_2^{2+}, O_2^-, O_2^{2-}.

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UNIT - V

STATES OF MATTER : GASES AND LIQUIDS

Introduction : Under suitable conditions of temperature and pressure almost all substances exist in three different states: Solid, Liquid and gas. Liquid and gas states can be considered as fluid state. It all depends on the existing force (s) present between the constituting particles (atoms, molecules or ions).

Inter molecular forces are the forces of attraction and repulation between interacting particles (atoms and molecules) Attractive intermolecular forces are known as vander Walls forces. It varies considerably in magnitude and include dispersion forces or Landon forces. Ion-dipole dorce is not vander walls forces.

Types of vander walls forces :

(i) **Dispersion forces or London forces :** Atoms are non-polar due to symmetric arrangement of electrons. No dipole moment. But a dipole may develope momentarily even is such atoms and molecules & it becomes unsymmetrical i.e. charge cloud is more on one side than other. Such instantaneous or tansient dipole distorts the electron density of the neighbouring atom close to it . The force between such temporary dipoles in known as London force / dispersion force. The attraction and the interaction energy $\alpha \frac{1}{r^6}$ where 'r' is the distance between two particles. Thus, these forces only at stoort distance (r<<) The magnitude of the force depends on polarisability of the particle.

(ii) **Dipole-dipole forces**

Partial charge (δ) on each end is much less than electronic charge $(1.6\times10^{-19}C)$. This intraction is stronger than London forces. The intraction energy between stationary polar molecules $\propto \frac{1}{r^3}$ and that between rotating polar molecule $\propto \frac{1}{2^6}$. The cumitative effect of London forces and dipole-dipole force increases the inter molecular forces.

(iii) **Dipole - Induced dipole forces .** Exist between one molecule with peramanent dipole-another lacking permanent dipole. Intraction energy $\propto \frac{1}{r^6}$. This depends on

(i) dipolement of the permanent dipole
(ii) Polarisability of the electrically neutral molecule
(Largersize)

Here also cumilative effect of dispersion forces and dipole - induced dipole interactions exist.

(iv) **Hydrogen bond :** It is special case of dipole-dipole force occurs where lighy polar N–H, O–H or H–F bonds are present. F(4.0), 0(3.5), N (3.0) are the most electronegative atoms. Cl (3.0) may also take part in H-bonding. Energy of H-bond varies between 10–100 kJ/mol. Strength of the hydrogen bond is determined by the coulombic interaction between the one pair electrons of the electronegative atom of one molecule & H-atom of other molecule of same or different compounds.

→ **Repulsive forces** : In addition to the inter molecular attractive forces there exists repulsive forces on one another. When molecules come closer repulsion between the electron clouds & that between nuclei of two molecules come into play. Magnitude of this force rise when the distance of separation decreases . This is the reason that liquids and solids are hard to compress.

Thermal energy. This arises from motion of its atoms and molecules. It is directly proportional to temperature. It is the measure of average K.E. of the particles of the matter is called **Thermal motion.**

→ Inter molecular forces vs thermal interactions :

Three states of matter are the result of balance between the intermolecular forces and the thermal energy of the molecules.

Predominance of intermolecular forces and thermal energy of a substance in three states depicted as follws :

The m.p. and b.p. can also be predicted from the intermolecular interaction. higher intermolecular force higher in the b.p..

The Gaseous state (Elementary gases 11 - Five diatomic and six - monoatomic)

→ **Characteristics of gases :**

(i) No definite shape and volume.
(ii) Expansibility and compressibility

(iii) Diffusivity
(iv) Low density
(v) Eexerts pressure
(vi) Homogeneity
(vii) High pressure below its critical temperature, gas can be liquified.
(viii) Colour : Most of the gases are colourless and all are transparent.

→ Meassurable properties of gases : Four, (i) mass (ii) volume (iii) pressure (iv) Temperature.

Gas laws :

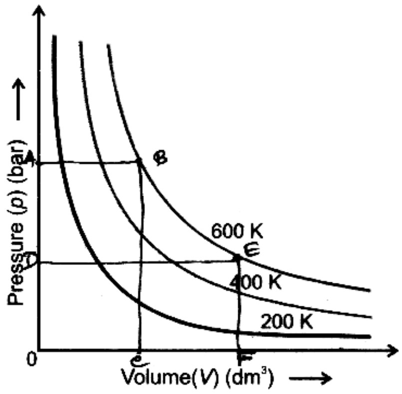
Boyle's law : Temperature remaining constant the pressure of a fixed amount (n = constant) of gas varies inversely with its volume.

i.e., $p \propto \frac{1}{v}$ when n & T are constant

$p_1v_1 = p_2v_2 = ... = K$ (constant)

Graphical verifications :

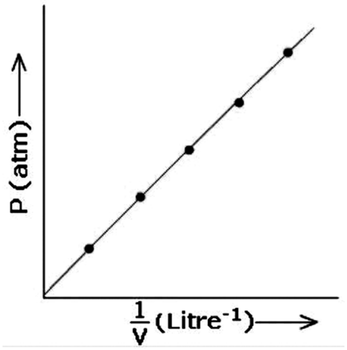
(i)



It is seen the area OABC = area ODEF indicating $P_1V_1 = P_2V_2$

(ii) Plot PV - P $T_3 > T_2 > T_1$
It indicates PV = constant for a given mass of gas at a given temperature.

(iii) Plot of P verses $\frac{1}{V}$



It indicates $P \equiv \frac{1}{V}$

All these plots are called isotherms i.e. at constant temperature.

→ P-density relation (a corollary of Boyle's law)

$$V \propto \frac{1}{P} \qquad \text{density (d)} = \frac{m}{v}$$

$$V \propto \frac{1}{d} \qquad d \propto \frac{1}{v}$$

i.e. $d \propto p$. Thus the density is directly proportional to pressure at a given temperature.

Charles's law. (Temperature - Volume relationship)

Statement : Presure remaining constant, the volume of a given mass of any gas increases or decreases by $\frac{1}{273}$ of its volume at 0^0C for each 1^0 rise or fall in temperature.

Derivation :

$$V \text{ at } 0^0C = V_0$$

$$\text{Volume at } 1^0C = V_0 + V_0 \times \frac{1}{273}$$

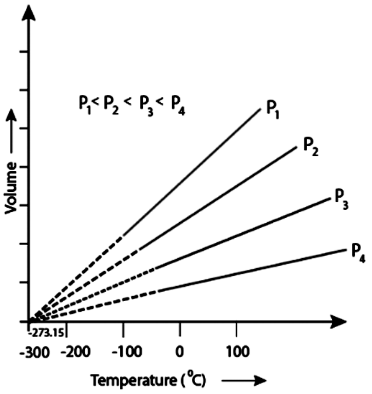
$$\text{Volume at } 2^0C = V_0 \times \frac{2}{273}$$

$$\text{Volume at } t^0C = V_0 + \frac{V_0}{273} \times t$$

$$\text{i.e, } V_t = V_0\left(1 + \frac{t}{273.15}\right)$$

$$V_{-273^0C} = V_0\left(1 + \frac{-273}{273}\right) = 0$$

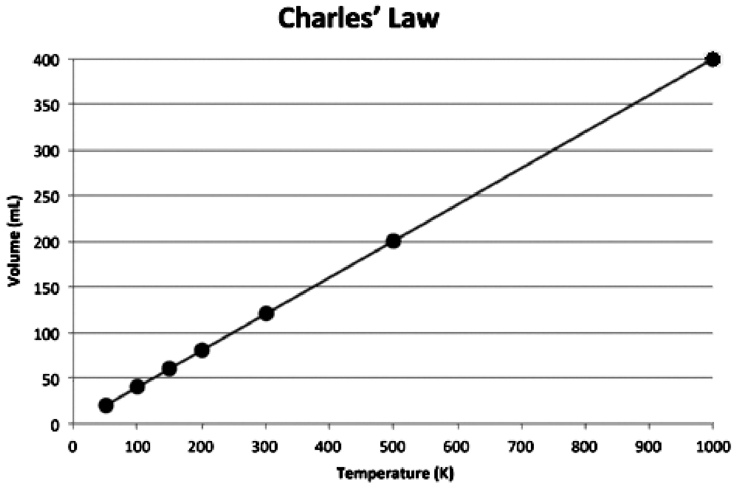
This defines absolute zero of temperature i.e., gas occupy no volume at -273^0C i.e. gases cease to exist in gaseous form / might be converted to liquid or solid.



Volume Vs Temperature graph (°C)

v-t plots are called isobars.

V-T plots are linear passing through origin.



Absolute scale of temperature.

– 273^0C is termed as absolute zero (O K)

$t^0C = (273 + t)K$

Boiling point of water = (273 + 100)K = 373 K

freezing point of water = (273 + 0)K = 273 K

Assume that at t_1^0C the volume is V_1 &

at t_2^0C the volume is V_2

$$V_1 = V_0\left(1+\frac{t_1}{273}\right)$$

$$V_2 = V_0\left(1+\frac{t_2}{273}\right)$$

$$\Rightarrow \quad \frac{V_1}{V_2} = \frac{273+t_1}{273+t_2} \quad \Rightarrow \quad \frac{V_1}{T_2} = \frac{T_1}{T_2} \Rightarrow \frac{V}{T}$$ constant, at agirum, P.

Let us write $T_{(t)} = 273+t$

i.e., $T_1 = 273 + t_1$

$T_2 = 273+t_2$

T is the temperature in kelvin scale.

Thus, $V \propto T$ at constant pressure Charle's in term of density.

For agiven mass, $V \propto \frac{1}{d}$

$$d \propto \frac{1}{T}$$

i.e., $d_1T_1 = d_2T_2$

* **Gay Lussac's law (P-T relationship)**

At constant volume , pressure of a fixed amount of a gas varies directly with temperature.

Like Charles' law $P_t = V_0\left(1+\frac{t}{273}\right)$

So $P \propto T$ or $\frac{P}{T} = \text{constant}$.

The P–T plots are isochores.

* **Avogadro's law** (Volume and amount, n relation)

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

$V \propto n$ when T & P are constant.

At STP (T = 273 K, P=1 bar) 1 mole of any gas occupies 22.4 L having 6.022×10^{23} molecules.

Ideal gas equation :

At constant, $T,\ _n{:}V \propto \frac{1}{p}$ Boyles' law

At constant p, n : $V \propto T$ Charles' law

At constant P and T, $V \propto n$ Avogadro's law.

$$V \propto \frac{nT}{P}$$

$$\Rightarrow \quad V = R\frac{nT}{P}$$

PV = nRT where R in the universal gas constant. This is called ideal gas equation.

Combined gas equation :

$$\begin{tikzcd}
\boxed{\begin{matrix} P_1 & V_1 \\ T_1 & n \end{matrix}} \arrow[r, "\text{Pressure changes}", "\text{Boyles'law}"', "\text{I}"{yshift=25pt}] & \boxed{\begin{matrix} P_2 & V^{/} \\ T_1 & n \end{matrix}} \arrow[r, "\text{Temperatures changes}", "\text{Charles'law}"', "\text{II}"{yshift=25pt}] & \boxed{\begin{matrix} P_2 & V_2 \\ T_2 & n \end{matrix}}
\end{tikzcd}$$

$$\text{I}: P_1V_1 = P_2V^{/},\ \text{So } V^{/} = \frac{P_1V_1}{P_2}$$

$$\text{II}\ \frac{V^{/}}{I_1} = \frac{V_2}{T_2}$$

Substituting $V^{/}$ value $\frac{P_1V_1}{P_2T_1} = \frac{V_2}{T_2}$ $\Rightarrow$ $\boxed{\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}}$ .... combined gas equation.

Alternate: (i) $d \propto P$

(ii) $d \propto \frac{1}{T}$

$$\Rightarrow \quad \frac{dT}{P} = \text{constant i.e. } \frac{d_1T}{P_1} = \frac{d_2T_2}{P_2}$$

$\rightarrow$ Calculation of density : $PV = nRT$

$$\Rightarrow \quad PV = \frac{w}{M}RT$$

$$\Rightarrow \quad P = \frac{w}{V} \times \frac{RT}{M}$$

$$\text{i.e.} \quad P = \frac{dRT}{M}$$

or $d = \frac{PM}{RT}$, This shows $\frac{dT}{P}$ = constant density at any temp (T) and pressure can be calculated.

* **Significance of R**

$$R = \frac{P \times V}{n \times T} = \left(\frac{\text{Force}}{\text{area}}\right) \times \frac{\text{area} \times \text{length}}{\text{no.of mole} \times \text{Abs.temp.}}$$

$$= \frac{(\text{force} \times \text{length})}{\text{no.of mole} \times \text{Abs.temp.}} = \text{work mol}^{-1}\ \text{K}^{-1}$$

Thus, R is the work done permole per degree temperature

Unit of R

$$R = 0.0821\ \text{L-atom . mol}^{1-}\ .\ \text{K}^{-1}$$

$$R = \frac{PV}{nT} = \frac{(76 \times 13.6 \times 981)\,\text{dynes} / \text{cm}^2 \times 22.4\ \text{cm}^3}{1\,\text{mole} \times 273\,\text{K}}$$

$= 8.314 \times 10^7$ erg. $\text{mol}^{-1}\ \text{K}^{-1}$

$= 8.314$ J $\text{mol}^{-1}\ \text{K}^{-1}$ (SI unit)

$= 1.99$ cal $\text{mol}^{-1}\ \text{K}^{-1}$ 1 cal = 4.182 J

R is pascal unit :

1 atm = $1.013 \times 10^5\,\text{Pa} = 1.013 \times 10^5\ \text{N m}^{-2}$

V = $22.4\text{L} = 22.4 \times 10^{-3}\ \text{m}^3$

$$R = \frac{PV}{nT} = \frac{1.013 \times 10^5\ \text{Nm}^{-2} \times 22.4 \times 10^{-3}\ \text{m}^3}{1 \times 273}$$

$= 8.314$ Nm $\text{mol}^{-1}\ \text{K}^{-1}$ $\therefore$ 1 N.m = 1 J

$= 8.314$ J $\text{mol}^{-1}\ \text{K}^{-1}$

$= 8.314$ Pa $\text{m}^3\ \text{mol}^{-1}\ \text{K}^{-1}$ Pa = Nm^{-2}

$= 8.314$ K Pa $\text{dm}^3\ \text{K}^{-1}\ \text{mol}^{-1}$ m^3Pa = N.m

K.Pa = kilopascal

* **Dalton's law of partial presure (1801)**

The total pressure exerted by a mixture of non-reactive gases is equal to sum of their partial pressure i.e. the pressure exerted by individual gas if present alone in the mixing container at that temperature.

$P_{total} = P_1 + P_2 + P_3 + \ldots\ldots\ldots$ (at constant T and V)

$P_{dry\ gas} = P_{total}$ Aqueous tension.

→ Partial pressure in terms of mole fraction :

Gas – 1 $p_1 = \frac{n_1RT}{V}$ V = Volume of the mixing container

Gas – 2 $p_2 = \frac{n_2RT}{V}$

Gas – 3 $p_3 = \frac{n_3RT}{V}$

Now as per the law :

$$P_{total} = p_1 + p_2 + p_3$$

$$= \frac{RT}{V}(n_1 + n_2 + n_3)$$

$$\frac{p_1}{p_{total}} = \frac{\frac{(n_1RT)}{V}}{\frac{RT}{V}(n_1 + n_2 + n_3)} = \frac{n_1}{n_1 + n_2 + n_3} = X_1$$

$$p_1 = X_1 \cdot P_{total}$$

Thus, partial pressure of any component (i^{th})

= X_i(mole fraction of that compont) × total pressure of the mixture.

HOME ASSIGNMENT

(a) What are the measurable properties of gases ?

(b) Identify the monoatomic and diatomic gases present in nature.

(c) O_2 is present in one litre flask at a pressure of 7.6×10^{-10} mm, of Hg, calculate the no. of oxygen molecules at 0^0C.

(d) Calculate volume of 1 gramhydrogen at 27^0C and 1 atm pressure.

(e) Find out the density of nitrogen at 27^0C and 2 atm pressure.

(f) What is the density of CO_2 at NTP in gram/L.

(g) 300 mlof N_2 at pressure 740 mm and 350 ml of oxygen at a presence of 600 mm are put together in one litre Flask. If the temperature is kept constant what will be the total pressure ?

(h) What is an ideal gas ? Derive an equation of state for it.

(i) 500 ml of O_2 is collected at 27^0C. If the volume is reduced to $\frac{1}{4}$ th its original volume, find the temperature to which the gas to be cooled.

(j) A given mass oxygen occupies 300 cm^3 at 27^0C. What is the volume at 0^0C, pressure remains constant ?

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KINETIC MOLECULAR THEORY OF GASES

(MICROSCOPIC MODEL OF GASES:)

(i) Gases consist of minute particles (atoms or molecules), the volume is much les in comparison to the volume of the container. These are considered as point masse with negigible volume.

(ii) There is no force of attraction between the gas particles at ordinary temperature and pressure.

(iii) These particles are always in constant and random motion. During motion they collide among themselves always and against the wall of the container. The collisions against the wall provide the pressure of the gas.

(iv) The collisions are elastic in nature i.e. there is no loss of energy during collision.

(v) Particles move in all possible direction in straight line. The direction changes after collision. The particles must have different speeds, which go on changing constantly. This results in considering mean velocity & mean kinetic energy. The average kinetic energy is directly proportional to absolute temperature. $KE \propto T$.

The average velocity = $Ca = \dfrac{n_1V_1 + n_2V_2 + n_3V_3 + ...}{n_1 + n_2 + n_3..... = N}$

Root mean square velocity = $\bar{c} = \sqrt{\dfrac{n_1V_1^2 + n_2V_2^2 + n_3V_3^2 + ...}{N}}$

Remember : Kinetic gas equation: $PV = \dfrac{1}{3} m N \bar{C}^2$

$$\bar{C} = \sqrt{\frac{3PV}{mN}} = \sqrt{\frac{3RT}{M}}$$

mN = molecular mass, M $\qquad = \sqrt{\dfrac{3P}{(mN/V)}} = \sqrt{\dfrac{3P}{D}}$

D = density of the gas.

C_a (average velocity) = $\sqrt{\dfrac{8RT}{\pi M}}$

C_P (most probable velocity) = $\sqrt{\dfrac{2RT}{M}}$

→ Relationship : $C_P : C_a ; \bar{C} = 1 : 1.128 : 1.224$

Average velocity, $C_a = 0.9213 \times \bar{C}(RMS)$

→ Deviation from ideal gas :

In actual practice no gas is 100% ideal or perfect. PV.P plot for different gases is insupport of it. PV–P should have been parallel to P-axis, but not a single gas is in order, How ever, the deviation is much less when $P \longrightarrow O$.

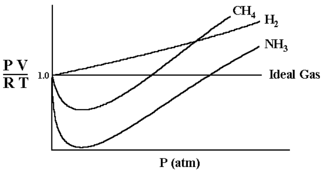
→ Cause of deviation :

(i) There exists intermolecular force of attraction between the real gas molecules.

(ii) Volume of individual real gas molecule cann't be neglected.

These two points are wrongly interpreted in the kinetic molecular theory, justifying ideal gas.

→ **Distinction between ideal gas and real gas :**

	Ideal gas		**Real gas**
(i)	The molecules are so small that volume is negligible.	(i)	Volume can't be neglected
(ii)	No intermolecular force of attraction.	(ii)	There exists intermolecular force of attraction attraction. So these gases can be liquified.
(iii)	PV – p plot isotherm parallel to pressure axis indicating PV = constant.	(iii)	
(iv)	The compressiblity factor(z) = $\frac{PV}{nRT}=1$	(iv)	Z value deriates from unity. At low pressure all gases shown Z = 1. At high pressure Z > 1. At an intermediate pressure Z<1. Gases behave ideal at a very low pressure and high temperature. In increase of presence 'Z'-value increases continuously.
(v)	Equation of state : PV = nRT	(v)	vanderWaals gas equation $\Rightarrow \left(P+\frac{an^2}{v^2}\right)\left(V-nb\right)=nRT$

→ Boyle temperature (T_B). The temperature at which Boyles' law is obeyed. above this temperature real gases show positive deviation from ideality and Z > 1.

$$\left(Z=\frac{V_{real}}{V_{ideal}}\right).$$

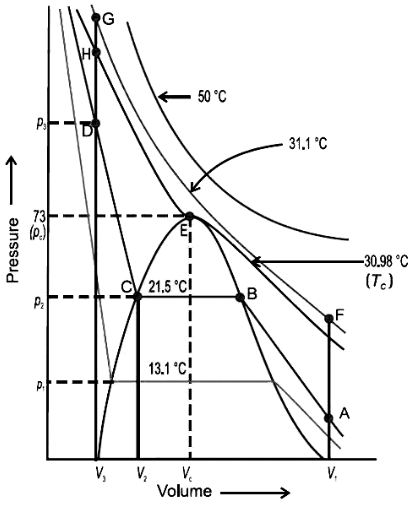
→ For H_2 and He, Z > 1 i.e. the gases are less compressible at all presure and at 0^0C. If the temperature is sufficiently low (below – 165^0C for H_2 and below – 240^0C for He) then same Z–P plot are shown by both these gases as for other gases.

→ Liquifaction of gases :

* PV isotherm of CO_2 shows that at 30.98^0C CO_2 remains gas upto 13 atm. presure. This temperature is called critical temperature (T_C of CO_2). This is the temperature above which gas Cann't be liquified what ever large pressure may be. The pressure at this temperature is called critical pressure (P_C). Less compresibility of liquid also is shown from the graph. Higher is the T_C greater is the ease of liquification.

e.g. T_C (NH_3) = 405.5 K T_C (CO_2) = 304.1 K.

NH_3 will liquify first as its T_c will reach first. liquifaction CO_2 needs more cooling.



HOME ASSIGNMENT

(a) Why does real gas deviate from ideal gas ?

(b) Mention the vander Waals equation for 1 mole of real gas.

(c) When do real gases tend to behave ideal ?

(d) What is comprenibility factor ? Discuss its value for H_2 and H_e.

(e) Write down the limitations of kinetic molecular theory of gases.

(f) Show that the excluded volume for each molecule will be 4 times its molecular volume when two molecules collide.

(g) Calculate rms velocity of nitrogen at 27^0C and 75 cm pressure. density of mercury = 13.6 gm/cm^3

(h) At what temperature the rms velocity of hydrogen will be same as that of oxygen at 30^0C ?

(i) What is an ideal gas ?

(j) Write the units of vander Waals constants ‘a’ and ‘b’. What happens when these values go on increasing ?

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LIQUID STATE OF MATTER .

Properties of liquid :

(i) Volume and shape : definite volume & but no definite geometrical shape.

(ii) Compressibility - almost in compressible.

(iii) Fluidity- possess the property of flowing.

(iv) Diffusivity - liquid also exhibit diffusion.

e.g. two miscible liquids.

(v) Evaporation : Easily evaporate on its surface.

(vi) Density : Due to weak intermolecular force it has less density than solid much & higher than gases.

(vii) Structure - Liquids possesse a distorted crystal lattice with a tendency to move in diferent direction. This is called semicrystalline state of liquids.

vapour pressure : The pressure exerted on the surface of liquid at a giiven temperature when both liquid & vapours are in a state of equilibrium, liquid $\rightleftharpoons$ vapour. This is called equilibrium V.P. or saturated V.P.

When the V.P. comes equal to atmospheric pressure, the liquid starts boiling and is called normal boiling point. If the pressure is 1 bar, the boiling point is called standard boiling point. ($99.6^0C = 372.6$ K) for water and its normal boiling point is $100^0C = 373$ K. At critical temperature density of liquid is equal to that of gas, the boundary between liquid-vapour dissappears.

* **Surface tension.**

Definition : It is the force in dyness acting at right angle to an imaginary line of unit length of a liquid.

Unit - dynes / cm or N/m.

→ Surface tension decreases with rise of temperature.

→ The magnitude of surface tension of a liquid depends on the attractive forces between the molecules.

→ Liquid tends minimise its surface area due to this e.g. liquid drop looks spherical.

* Viscosity - It is a measure of resistance to flow which arises due to the internal friction between layers of liquids (fluid) as they slip past one another while liquid flows. Upper layer has greater flowing tendency than its adjacent one.

$$\xrightarrow{\qquad\qquad\quad} u + du$$

$$\xrightarrow{\qquad\quad} u$$

$$\updownarrow dz$$

$$\xrightarrow{\quad} u - du$$

Velocity gradient = $\frac{du}{dz}$

Force, $f \propto A$ (area of contact)

$$f \propto \frac{du}{dz}$$

$f = \eta A \frac{du}{dz}$ 'η' is called coefficient of viscocity.

thus, η is force per unit area of cross section to have a unit difference of velocity when the subsequent layers are at unit distance apart.

* SI unit of viscosity : $N.s.m^{-2}$ = pascal.s = 1 Kg m^{-1} s^{-1}

poise (in CGS unit) = 10^{-1} Kg m^{-1} s^{-1}

= 1 gram cm^{-1} s^{-1}

→ Viscosity decreases with rise in temperature

→ Greater the inter-molecular force of attraction greater in the ciscosity. e.g $\eta_{glycerol} > \eta_{glycol}$

→ Viscosity increases with the increase in brancling of carbon chain in case of organic liquids.

HOME ASSIGNMENT

(a) Arrange the liquids in order of increasing viscosity :

Water, ethanol, glycerol, ethylene glycol.

(b) Explain the following :

(i) Surface tension decreases with rise of temperature.

(i) Conc. H_2SO_4 is a viscous liquid.

(iii) It is difficult to cook on the hill top.

(iv) Wet clothes dry quickly is winter season.

(v) Window glasses thickens at the bottom in old buildings.

(c) Fill in the gaps :

(i) Unit of ' η ' (eta) in SI unit is _____________.

(ii) Poise is the unit of ____________.

(iii) Vapour pressure rises with rise of ___________.

(iv) Normal boiling point of water is __________ while standard boiling point is ______.

(v) At standard boiling point the pressure is _________.

(vi) Critical temperature of CO_2 is _________ K.

(vii) The temperature at which liquid and its vapour have same density is called ______.

(viii) Liquid rises in the capillary due to its ________.

(ix) The internal resistance to flow possesed by liquid is called its _______.

(x) The surface a mercury in a glass tube is _______.

L-52 and 53

UNIT - VI

CHEMICAL THERMODYNAMICS

Introduction :

→ The branch of science which deals with the study of different forms of energy and quantitative relationship between them is known as thermodynamics (Thermo=heat, dynamics = in motion resulting into mechanical eork) → It deals with chemical reactions & the ebergy charge accompanying them. On this basis reactions are two types : (i) exothermic (heat is given out) (ii) endo thermic heat is absorbed. e.q. Decomposition of NH_3.

→ The laws of thermodynamics deal with energy changes of macroscopic systems involving a large no. of molecule at macroscopic properties like prescribe and temperature.

* **Basic terms and Concepts :-**

→ Syste and surrounding : A system refers that part of universe in which observations are made and remaining universe constitute the surroundings.

→ The wall that separates the system from the surrounding is called boundary through which matter and energy can flow.

sustem + surrounding = universe

→ Types of system

(a) **Open system :** where both matto and energy exchange between system and surrounding.

e.g. reaction in a test tube.

(b) **Closed system :** No exchange of matter but exchange of energy. e.g. matter in a closed vessel made of conducting material.

(c) **Isolated system :** Neither exchange of matter of energy with the surounding.

e.g., chemical reaction in a themosflask.

→ The state of the system (state variables) i.e. the conditions of the system which is described is terms of the certain measurable properties like P, V, T as well as composition of the system (no. of moles) etc. variables like.P, V, T are called state variables state function. A process is said to occur when the state of the system changes. The first state is called initial state reactant and last state is called find state (product).

→ **Internal energy : (state function)**

Chemical system loses (exothermic) or gains (endothermic) energy which repesents the total energy. It may be chemical, electrical, mechanical or any other type of energy. Thus sum of all types of energy passessed by the system is called internal energy (U).

→ Change of internal energy ((ΔU) the exact value of 'U' by a substance can't be determined as it's impossible to determine accurates most contributing quantities like vibrational, rotational, transloational, electronic etc, but the energy accompany the process, the change is internal energy (ΔU) can be determined accurates.

$(\Delta U) = U_2 - U_1$ U_2 = energy possessed by the system in find state (product)

U_1 = energy passed is initial state (reactant)

→ The internal energy depends on quantity of the substance hence extensive in nature.

→ The internal energu of ideal gases in a function of temperature only, thus for isothermal process (T = constant) $(\Delta U)_T = 0$

→ sign of ΔU : For exothermic process $U_2 < U_1$ is $\Delta U = U_2 - U_1 = -ve$.

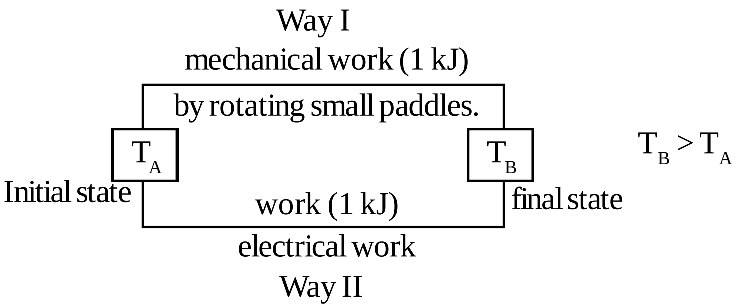
For endothermic process $U_2 > U_1$ is $\Delta U = U_2 - U_1$ = positive.

→ $\Delta U = q_{(v)}$ ie quantity of heat absorbed or evolved permole at constant volume.

→ It is a state function depending on initial and find states.

→ Unit of ΔU = kJ/mol.

Work :



Thus, irrespective different ways (way I and way II)

Same change of state, ΔU occurs. Thus ΔU does not depend on both.

→ Mechanical work = Force × desplacement
= Prefix × (area × displacement)
= Pressure × Volume

→ Sign of work. Work done on the system i.e., **Compression**.

(SI convention) carries **positive sign,** $w = p\,\Delta\,v$

In case of expansion work done by the system i.e., it carries negative sign.

$$w = -p\,\Delta\,v$$

→ Unit of w = evg (w) Joul = 1 Joul = 1 Nm = kg m^2 s^{-2}.

→ Derivation of the expresion $W_{rcv} = -2.303\ nRT\ \log\dfrac{V_f}{V_i}$ (isothermal reversible expansion)

For isothermal irreversible change = $-P_{ext}(v_f - v_i)$

→ For free expansion $P_{ext} = 0$, No work is done.

Heat : Just like work, heat is another mode of energy exchanged between the system and surrounding as a result of difference of temperature occurs. Both heat (q) and work (w) appear only at the boundary of the system.

→ Sign of 'q' : Exothermic process, q =–ve. If heat is absorbed i.e., exothermic q = positive.

Unit of 'q' = cal, SI unit = Joul

1 cal = 4.184 J

w and q are path functions (Not depending on initial and final state)

HOME ASSIGNMENT

1. **(a)** The SI unit of work is __________. [1

(b) show that work is a path function write internal energy is a state function. [3

(c) What do you mean by mechanical work? [2

L-54.

* **Difference betwen heat and work :** When heat is supplied to ages randomness in glass in different directions. However, when work is done on the system, then initially the molecules start moving down in the direction of piston. Thus, heat is random form of energy, work in an organised form of energy.

* **Macroscopic properties :**

→ **(i)** extensive properties - Depending on quantity of the substance e.g. mass, volume, heat capacity, enthalpy, internal energy, entropy.

→ **(ii)** **Intensive properties -** depending on nature of the substance and independent of quantity of the substance.

Example : Pressure, temperature, refractive index, viscosity, surface tension, specific heat, boiling point, melting point etc.

→ An extensive property may become intensive by specifying unit amount e.g. mass is extensive but mass per unit volume is intensive.

→ an extensive property is additive in nature but intensive property is not.

* State function a physical quantity is said to be state function it its value depends on the state of the system and does not depend on path / way by which the change occurs.

Example : A person standing on the roof of a five storeyed building has a fixed value of potential energy irrespective of the fact that he reached their by stairs or lift. Thus, P.E. of the person is a state function, but the work done by the person by legs to reach the same height is not same in two cases (stairs / lift). hence work is a path function.

Ex. Properties of system depending only initial final slats _____

ΔU, ΔH, ΔS, ΔG etc.

Problems :

(1) One mole of an ideal gas contained in a bulb of 10 L capacity at 1 atm is called to enter into an evacuated bulb of 100 L capacity. [Ans - 0]

(2) One mole of a gas is allowed to expand from a volume of 5 litres against external pressure of 1 atm. [1 L. atm = 101. 3 J] [Ans = -405.2 J]

(3) Calculate the maximum work obtained when 0.75 mole of an ideal gas expands isothermally and reversibly at 27^0C from a volume of 15 L to 25 L. [Ans = –955.5 J]

HOME ASSIGNMENT :

(1) Put the symbol (e) for extensive and (i) ntensive property is the following :

Vapour pressure at 298 k, density, specific quantity, no. of moles refractive index, mass, enthalpy, Gibbs free energy, random ness of a system, internal energy.

(2) Calculate the work done when 1.0 mole of water and 373 K vaporises at 1-atom pressure. Assume ideal gas behavious & neglect the volume of water.

(3) Why work and heat have identical unit ?

L -55 **First law of thermodynamics** (Law of conservation of energy)

→ The energy of an isolated system is constant.

or

Energy can neither be created nor destroyed although it may be converted from one form to arding.

Observation from our experience :

→ In the operation of an electric fan the electrical energy is converted to mechanical work which moves the blades.

→ In a heater electrical energy converted to heat.

→ Mathematical expression : The internal energy can be increased in two ways :

(i) By applying heat to the system.

(ii) by doing work on the system.

$$\boxed{U_1} \xrightarrow[\text{(Heat absorbed)}]{+q} \boxed{U_1 + q} \xrightarrow[\text{work done on the system}]{+(w)} \boxed{\begin{matrix} U_1 + q + w \\ = U_2 \end{matrix}}$$

initial state Final state

$$U_2 = U_1 + q + w$$

$$\boxed{\Delta U = q + w}$$

If in the second step work is done by the system (-w)

i.e., $w = -P\Delta V$

$$\Delta U = q - P\Delta V$$

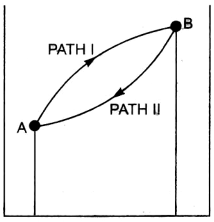
$\boxed{q = \Delta U + P\Delta V}$, at constant volume $\Delta U = 0$ i.e., $\boxed{q_V = \Delta U}$

Thus, (i) q and w are not state function but $q + w = \Delta U$ is a state function.

(ii) For an ideal gas undergoing an isothermal change, $\Delta U = 0$. hence q $= -w$

Heat absorbed by an ideal gas (system) is equal to work done by the system (expansion).

(iii) ΔU is defined as q_v i.e, 'q' absorbed or evolved at instant volume is a state function :.



Internal energy as a function of state

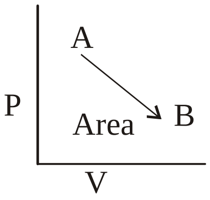
$$A \xrightarrow{\text{Path.I}} B,\ \Delta U$$
$$B \xrightarrow{\text{Path II}} A,\ \Delta U\ (\text{say})$$

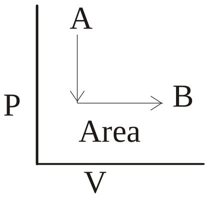
If $\Delta U > \Delta U'$ same energy is created. This is against first law. hence ΔU must be equal to ΔU '.

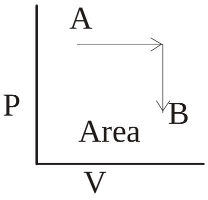
It only depends initial (A) and find state (B), but not on the path.

→ Work (w) and heat (q) are not state functions.

Work of expansion in differ path is different as plotted.







The area, $P\Delta V$ it work done is different when different paths are followed .

$$q = \Delta U - w$$

ΔU is a state function w is a path function, hence 'q' is also not a state function.

* **Enthalpy (Heat content)**

$$\boxed{\begin{array}{l} T \\ U_1 \\ V_1 \end{array}} \xrightarrow{q(p)} \boxed{\begin{array}{c} T \\ U_1 + q_p \end{array}} \xrightarrow[\text{by the system with increase of volume from } v_2 \text{ to } v_2]{\text{work done}(-w)} \boxed{\begin{array}{l} T,\quad U_2 \\ U_1 + q - w = U_2 \\ V_2 \end{array}}$$

initial state

Now $U_2 = U_1 + q_p - w$

$= U_1 + q_P - P(V_f - V_i)$

$= U_1 + q_P - PV_2 + PV_1$

v_1 = initial volume

v_2 = final volume

$v_2 > v_1$

$\Rightarrow \left(U_2 + PV_2\right) = \left(U_1 + PV_1\right) + q_p$ .... (1)

Let is define another state function i.e., U + PV = H

So $H_1 = U_1 + PV_1$ (at constant pressure)

$$\underline{H_2 = U_2 + PV_2}$$

$$\underline{H_2 - H_1 = U_2 - U_1 + P\left(V_2 - V_1\right)}$$

$$\Rightarrow \Delta H = \Delta U + P\Delta V$$

$$\boxed{\Delta H = \Delta U + \Delta n_g RT}$$

Δn_g = difference is no of moles of gas.

e.g $H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)}$ $\Delta n_{(g)} = 0$

In this case $\Delta H = \Delta U$

From equation (1)

$H_2 = H_1 + q_p$

i.e., $\boxed{q_p = \Delta H}$

Thus, change in enthalpy is the quantity of heat evolved or obserbed at constant pressure.

→ Sign and units of ΔH

For exothermic q_p is negative hence $H_2 < H_1$ i.e., $H_2 - H_1$ = –ve.

→ UNIT - Joul/mole

HOME ASSIGNMENT

(i) What is difference between heat absorbed at constant pressure and that at constant volume ?

(ii) Find a relationship between ΔH and ΔU for the reaction :

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

(iii) In internal energy (ΔU) for the reactoin :

$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O(\ell)$ is – 885 kJ / mol at 298 K. What is its ΔH value ?

(iv) Correct the following stataements

(a) ΔH and ΔU are state functions

(b) ΔH is intensive while ΔU is extensive

(c) The absolute value of internal energy can be determined

(d) In a cyclic process both ΔH and $\Delta U = 0$

(e) Design a simple experiment to show volume is an extensive while temperature is an intensive property of a system.

L-56. Specific heat : It is the amount of heat required by 1 gram substance to raise its temperature through 1^0C.

→ Molar heat capacity - if 1 mole of substance is taken.

→ Heat capacity (C) = $\frac{q}{T_2 - T_1} = \frac{q}{\Delta T}$

$$\boxed{q = m\ C\Delta T}$$

Unit of molar specific heat J/mol/K

→ The increase of temperature (ΔT) is directly proportional to the quantity of heat absorbed.

→ Types of heat capacity :

Heat capacity at constant volume → C_v

Heat capacity at constant pressure → C_p

→ Definition

→ We know $\Delta U = q_v$

$$C_v = \frac{\Delta U}{\Delta T} \quad \text{i.e.,} \left(\frac{\partial U}{\partial T}\right)_v$$

Similarity $C_p = \frac{\Delta H}{\Delta T}$ i..e, $\left(\frac{\partial H}{\partial T}\right)_p$ $\left[\text{as } \Delta H = q_p\right]$

→ Relationship between C_p and C_V for ideal gas :

For one mole of ideal gas

$$\Delta H = \Delta U + \Delta(PV)$$

$$= \Delta U + \Delta(RT)$$

$$\Delta U = \Delta U + R\Delta T$$

From above - $C_P\Delta T = C_V\Delta T + R\Delta T$

$\Rightarrow$ $C_P = C_V + R$

i.e, $(C_P - C_V) = R$

→ Measurement of ΔU and ΔH

Calorimetry (Bomb calorimeter)

Principle : → $\Delta U = q_{(V)}$ where $q_V = C_V.m\Delta T$, m = mass of the substance taken,

C_V = heat capacity of the calorimeter.

→ A combustible substance is burnt is pure O_2 supplied into a steel bond (constant V)

→ Measurement of ΔH

→ $\Delta H = q_P$. Bomb calorimeter is maintained at constant pressure i.e., 1 atm. plessure.

Problem : (a) A piece of Al metal weighing 3 gram requires 5.4 J of heat to raise temperature from 298 K to 300 K. Calculate heat capacity, capacity of Al.

$$\text{Heat capacity} = \frac{5.4\,\text{J}}{2\,\text{K}} = 2.7\,\text{J}\,\text{K}^{-1}$$

$$\text{Specific heat } = \frac{5.4\,\text{J}}{2\,\text{K} \times 3\text{g}} = 0.9\,\text{J}\text{g}^{-1}\text{K}^{-1}$$

$$\text{Molar heat capacity - 3 gram } = \frac{3}{27}\,\text{mol}$$

$$= \frac{5.4\,\text{J}}{2\,\text{K} \times \frac{3}{27}\,\text{mol}} = 24.3\,\text{J mol}^{-1}\,\text{K}^{-1}$$

(b) 1 gram of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atm. Pressure according to the equation :

$$C_{(\text{graphite})} + O_{2(g)} \longrightarrow CO_{2(g)}$$

During reaction temperature raises from 298 K to 299 K. If the heat capacity (C) of the bomb calorimeter is 20.7 kJ / K.

Calculate ΔH and ΔU.

$$\Delta U = q_v = m \times C_v \times \Delta T$$

$$= 1\text{gram} \times 20.7\,\text{kJ/K} \times 1.\text{K}$$

$$= 20.7\,\text{kJ}.$$

As its exothermic, $\Delta U = -20.7$ kJ

For 12 gram of graphite $\Delta U = -20.7 \times 12 = 248.4$ J/mol

In the above reaction $\Delta n_g = 0$

$$\Delta H = \Delta U = -2.48 \times 10^2\,\text{kJ/mol}.$$

HOME ASSIGNMENT

(a) What is the value of difference between C_P and C_V in SI Unit ?

(b) Why molar heat capacity is greater than specific heat capacity ?

(c) The unit of molar heat capacity is ____________ .

(d) What is amount of heat needed to raise the temperature of 10 gram of iron from 25^0C to 500^0C if specific heat capacity of iron is 0.45 J gram^{-1} K^{-1}.

L - 57.

HESS'S LAW OF CONSTANT HEAT SUMMATION :

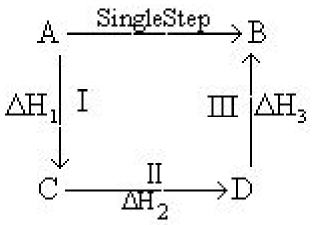
Statement :

If a reaction takes place is several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the over all reaction may be divided at the same temperature.

or

The heat charge of a reaction is same whether the reaction takes place in one step or in several steps.

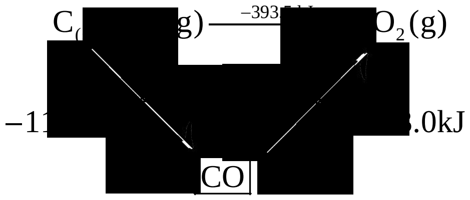
Explanation :



Steps where the intermediates are C and D.

It is seen $\Delta H = \Delta_1^H + \Delta H_2 + \Delta H_3$

Example **:** Formation of CO_2 on burning 'C'



[redacted]

→ **Significance :**

→ This is in accordance with first law. Energy is fixed for a particular reaction.

→ ΔH value is a state function i..e, its value depends on initial (reactant) & final value (product) but independent of whether it take place in one way or in several ways.

→ **Applications :** Calculation $\Delta_r H, \Delta_f H, \Delta_{transition} H.$

Some definitions : Standard state of a substance at a specified temperature (298 K) is its pure form at 1.0 bar.

→ **Standard enthalpy of reaction :** $\Delta_r H^0$ is the enthalpy change for a reaction when participating substances (reactants and products) are in their standard staes.

$$\Delta_r H^0 = \sum_i a_i H^0{}_{products} - \sum_i b_i H_{reactants}$$

a_i & b_i arestoichiometric coefficients of reactants and products respectively.

Enthalpy of pure element (in standard state) taken as zero.

Example : $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O(l)$

$$\Delta_r H = \left[H_{CO_{2(g)}} + 2H_{H_2O(\ell)}\right] - \left[H_{CH_{4(g)}} + 2H_{O_2(g)}\right]$$

→ Standard enthalpy of formation $\overset{0}{\Delta_f} H$ **:** It is change in enthalpy in the formation of one mole of a compound from its constituting elements.

e.g. $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O + 285.8\ kJ/mol$

i.e., $\Delta_f H^0 = -285.8\ kJ/mol$

$$C_{(s)} + 2H_{2(g)} + \frac{1}{2}O_2 \longrightarrow CH_3OH + 238.86\,kJ/mol$$

$$\Delta_f H^0 (CH_3OH) = -238.86\,kJ/mol$$

It shows that here heat of reaction is same as heat of formation.

→ **Application :** To calculate the heat of reaction.

$$\Delta_r H = \sum \Delta_f H_{(Products)} - \sum \Delta_f H_{reactants}$$

e.g., $C_2H_5OH_{(\ell)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(\ell)}$

$$\Delta_r H = \left[2\Delta_f H(CO_2)_g + 3\Delta_f H\left(H_2O\right)_{(\ell)}\right] - \left[\Delta_f{}^{H}C_2H_5OH + 3\times\Delta_f H\left(O_2\right)\right]$$

$$= -1367 \text{ kJ/mol}$$

Hence heat of reaction is same as heat of combustion of ethanol. –ve sign indicates the reaction is exothermic in nature. The balanced chemical equation with the value of $\Delta_r H$ is called **thermochemical equation.**

Standard enthalpy of combustion : $\left(\Delta_C H^0\right)$ it is the heat evolved or enthalpy change occurs during combustion of one mole of substance at the specified temperature.

$$C_4H_{10} + \frac{13}{2}O_{2(g)} \longrightarrow 4CO_{2(g)} + 5H_2O_{(\ell)}$$

(Cooking gas)

The heat of reaction in same as heat of combustion. $\Delta_C H^0 = -2658.0 \text{ kJ / mol}$

Standard enthalpy of sublimition

It is the change in enthalpy when 1 mole of solid sublimes or converts to one mole of vapour at a constant temperature under standard pressure 1 bar.

$\Delta_{sub.} H^0 = \text{positive}$

$$\Delta_{sub.} H = \Delta_{fus.} H + \Delta_{vap.} H \,.$$

→ **Enthalpy change during phase transition :**

Solid $\xrightarrow{\Delta_{fus}H}$ liquid $\xrightarrow{\Delta_{vap}H}$ vapour

Statement : (i) The enthalpy change (heat required) in melting one mole of solid to one mole of liquid at its melting point.

$$H_2O(s) \longrightarrow H_2O(\ell) \qquad \Delta_{fus.} H = +6.0 \text{ kJ / mol}$$

(ii) Enthalpy of vaporisation, $\Delta_{vap.} H^0$.

Statement : Example $H_2O(\ell) \xrightarrow{+40.79 \text{ kJ/mol}} H_2O_{(vap)}$

$$\Delta_{vap.} H = +40.79 \text{ kJ / mol}$$

(iii) Solid $\xrightarrow{\Delta_{sub.}H}$ Vapour

* Problems (From Text)

HOME ASSIGNMENT

(a) Provide sign of ΔH values of ____________ .

heat of sublimation, $\Delta_r H, \Delta_{fus} H,\ \Delta_{vap} H,\ \Delta_f H$.

(b) Choose the correct statement (&) from the following :

(i) It is possible to design a machine which would work continuously without consuming energy.

(ii) 1 Joul = 0.2390 calories (iii) Heat content is measured using bomb calorimeter..

(c) a mole of 'A' reacts with b moles 'B' to form 'c' mol of C. In the reaction 'Q' Joul of heat is evolved. Write the thermo chemical equation of such reaction.

(d) Heat of combustion of $C_6H_6(\ell)$ is 3267.0 kJ/mol. Calculate the $\Delta_f H^0$ of benzene if $\Delta_f H^0 CO_2 = -393.5\,kJ/mol$ and $\Delta_f H^0 (H_2O) = -285.83\,kJ/mol$.

(e) Calculate the enthalpy change accompanying the transformation of C (graphite) to C (diamond). Given enthalpy of combustion of graphite and diamond are 393.5 and 395 kJ/mol respectively.

L-58 :

→ **Enthalpy of ionisation, $\Delta_i H$:** It is the energy required or change of enthalpy occurs on transforming 1.0 mole of atom to 1 mole of ions in gaseous state.

Successive $\Delta_i He$ values :

$$Mg(g) + \Delta_i H_1 \longrightarrow Mg^+_{(g)} + e^- \quad \Delta_i H_1 = 737.76\ kJ/mol$$

$$Mg^+(g) + 1450.73\,kJ \longrightarrow Mg^{2+}_{(g)} + e^- \quad \Delta_i H_2 = 1450\,kJ/mol$$

Thus $\Delta_i H_2 > \Delta_i H_1$.

Ref : Unit - III

→ **Enthalpy of solution, $\Delta_{sol.} H$:** It is the enthalpy change (i.e., amount of heat evolved or absorbed) when 1.0 mole of substance is dissolved in such a large amount of solvent that further addition of solvent does not produce any more heat change.

$$CuSO_4.5H_2O + water \longrightarrow CuSO_4(aq), \Delta H = 11.7\,kJ$$

$$CuSO_4 + water \longrightarrow CuSO_4(aq), \Delta H = -66.5\,kJ$$

$$CuSO_4(s) + 5H_2O \longrightarrow CuSO_4.5H_2O$$

$$\Delta H = (-66.5 - 11.7) kJ = -78.2\ kJ$$

This is called **enthalpy of hydration** of $CuSO_4$. i.e., the heat change to prepare hydrated salt from one mole of anhydrous salt.

In ionic compound, the lattice breakes & the ion gets hydrated i.e. the ionic compound dissolved when hydration energy exceeds the lattice energy. Hydration of ions arises due to ion-dipole attraction.

Diagramatically Δ_{soln} of $AB_{(S)}$ (an ionic compound)

$$\begin{tikzcd}
AB(s) \arrow[r, "\Delta_{sol}H"] \arrow[d, "\Delta CaH"] & A^+_{(aq)} + B^-(aq) \\
A^+_{(g)} + B^-_{(g)} \arrow[ur, "\Delta_{hyd}H"] &
\end{tikzcd}$$

As per Hess's law : $\boxed{\Delta_{soln}H = \Delta_{lattice}H + \Delta_{hyd}H}$

Mostly its endothermic in nature & solubility increases with water.

$\Delta_{lattice}H$ is the energy required to break one mole of ionic compound(s) to constituting ions in gaseous state. This can be calculated using Born-Haber cycle.

Example : $\Delta_{lattice}H$ of NaCl

$$\mathrm{Na(s)} + \frac{1}{2}\mathrm{Cl_2(g)} \xrightarrow{\Delta_f H} \mathrm{NaC\ell(s)}$$

$$\begin{array}{lllll|l}
+ & \downarrow \Delta^{H}_{Sub} & (+)\downarrow \frac{1}{2}\Delta^{H}_{bond} & & & \\
 & \mathrm{Na_{(g)}} & \mathrm{Cl_{(g)}} & & & \Delta_{Lattice}H \\
-\bar{e} & \downarrow \Delta_i H & (-)\downarrow \Delta_{eg}H & (-) & & \\
 & \overset{+}{\mathrm{Na}}\mathrm{(g)} & + \ \mathrm{Cl^-_{(g)}} & \longrightarrow & &
\end{array}$$

$\Delta_{eg}H$ = electron gain enthalpy.

(Ref. Periodic classification of elements)

As per law of conservation of energy –

$$\Delta_f H = \Delta_{sub.}H + \Delta_i H + \frac{1}{2}\Delta_{bond}H + \Delta_{eg}H + \Delta_{lattice}H$$

From this lattice energy can be calculated.

→ **Heat of dilution :** The enthalpy change per mole of solute when a solution is greately diluted.

→ **Enthalpy of atomisation :** It is the enthalpy change accompanying the total separation of all atoms in a chemical substance (element on compound) in gaseous state. It is always endothermic i.e., $\Delta_a H = +ve$.

Example : (i) $\mathrm{H-H(g)} \longrightarrow \mathrm{2H(g)}$ $\Delta_a H = 435.0\ \mathrm{kJ/mol}$

1 mole of molecule → 2 moles of atoms

(ii) $CH_{4(g)} \longrightarrow C_{(g)} + 4H_{(g)} \quad \Delta_a H = 1665 \text{ kJ/mole}$

(iii) $Na(s) \longrightarrow Na(g) \quad \Delta_a H = 108.4 \text{ kJ/mol}$

Here $\Delta_a H = \Delta_{subl.} H$

* **Enthalpy of bond dissociation :** $(\Delta_{bond} H)$

Energy needed(+) to break a bond while energy. released (–) when a bond is formed. Thermo chemical reaction involves breaking and making of bonds. It involves two different terms :

(i) bond dissociation enthalpy

(ii) mean bond enthalpy

Diatomic molecules :

$$H_{2(g)} \longrightarrow 2H_{(g)} \quad \Delta_{H-H} H^0 = 435 \text{ kJ/mole}$$

$$\text{Enthalpy of formation of } H_{(atom)} = \frac{435}{2} \text{ kJ/mol}$$

$$O_{2(g)} \longrightarrow 2O_{(g)} \qquad \Delta_{O=O} H^0 = 428 \text{ kJ/mol}.$$

Polyatomic molecules :

$$CH_{4(g)} \longrightarrow CH_{3(g)} + H_{(g)} \qquad \Delta_{bond} H^0 = +427 \text{ kJ/mol}$$

$$CH_{3(g)} \longrightarrow CH_{2(g)} + H_{(g)} \qquad \Delta_{bond} H^0 = +439 \text{ kJ/mol}$$

$$CH_{2(g)} \longrightarrow CH_{(g)} + H_{(g)} \qquad \Delta_{bond} H^0 = +452 \text{ kJ/mol}$$

$$CH_{(g)} \longrightarrow C_{(g)} + H_{(g)} \qquad \Delta_{bond} H^0 = 347 \text{ kJ/mol}$$

$$CH_{4(g)} \longrightarrow C_{(g)} + 4H_{(g)} \qquad \Delta_a H = +1665 \text{ kJ/mol}$$

So the mean bond enthalpy of C–H bond ———

$$\Delta_{C-H} H^0 = \frac{1665}{4} = 416 \text{ kJ/mol}$$

→ **Application :** Calculation of standard enthalpy of reaction, $\Delta_r H^0$

i..e, = $\sum \text{B.E(reactants)} - \sum \text{BE(product)}$

→ Determination of Bond enthalpy : This can be calculated by considering.

Heat of formation, $\Delta_{subl} H$, $\Delta_a H$ etc. applying Hess's law.

→ The bond enthalpy of diatomic molecular like HCl, HF etc. can be calculated directly from experiments or may be calculated from bond enthalpies homonuclear diatomic molecules.

HOME ASSIGNMENT

(a) Lattice energy of an ionic compound can be calculated using the principle of ______ cycle.

(b) Heat of sublimation of 'K' is same its enthalpy of ___________ .

(c) Arrange the following in order of their increasing bond dissociation enthalpy.

$$N_{2(g)}, O_{2(g)}, F_{2(g)}, Cl_{2(g)}.$$

(d) Identify the factors affecting the solubility of ionic compounds.

(e) Why do many fluoride find to be less soluble than corresponding chlorides ?

(f) Can it be possible to determine lattice enthalpy directly by calorimetry ?

L-59. → **Factors effecting bond dissociation enthalpy :**

Bond length, bond order, resonance, electronic repulation $\left(\begin{matrix}\text{B–E} \\ \text{F–F}\end{matrix} < \begin{matrix}\text{BE} \\ \text{Cl–Cl}\end{matrix}\right)$, polarity (% of ionic character)

→ Discussion through numericals.

1. Calculate the enthalpy change when 2.38 g of CO vaporise at its normal boiling point. Given that $\Delta_{vap}H_{(CO)} = 6.04\,kJ/mol$
2. Calculate the enthalpy of hydrogenation of C_2H_4 (ethylene), given that enthalpy of combustion of ethylene, hydrogen and ethane are –1410.0, –286.2 and –1560.6 kJ/mol respectively at 298 K.
3. The thermite reaction used for welding of metals involves the reaction :

   $$2Al_{(s)} + Fe_2O_{3(s)} \longrightarrow Al_2O_3(s) + 2Fe(s)$$

   What is the ΔH^0 at 298 K for this reaction. Given that $\Delta_f H^0$ of Al_2O_3 and Fe_2O_3 are –1675.7 kJ and – 828.4 kJ per mol respectively.
4. The enthalpies of combustion of ethanol, carbon and hydrogen are –1380.7 kJ, –394.5 kJ and –286.6 kJ/mol respectively, Calculate the enthalpy of formation of ethanol.
5. Calculate the bond enthalpy of HCl. given that bond enthalpies of H_2 and Cl_2 are 430 kJ and 242 kJ per mole respectively. $\Delta_f H(HCl) = -91\ kJ/mol$.
6. Calculate the bond enthalpy of C–H bond, given that heat of formation of CH_4, heat of sublimation of $C_{(s)}$ and heat of dissociation of H_2 are – 74.8, –719.6 and 435.4 kJ/mol respectively.
7. The bond dissociation energy of C–C 347.3, C=C – 615 and C–H 416.2. The experimental bond dissociation energy of benzene is 5535.1 kJ/mol. Calculate its resonance energy.

HOME ASSIGNMENT

a. For one mole of NaCl (s) lattice enthalpy = +788 kJ/mol and $\Delta_{hyd.}H^0 = -784$ kJ/mol. Calculate its heat of solution.

b. What are thermochemical reactions ?

c. Identify at least four different types of thermochemical reaction where ΔH values are exothermic.

d. Fluorine has lower bond dissociation enthalpy from chlorine - explain.

e. Calculate the enthalpy change for the reaction :

$H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)}$, given that bond dissociation enthalpy of H–H, I–I and H – I are 433, 151 and 299 kJ/mol respectively.

f. Why certain reactions are exothermic in nature ?

L-60. Scope of second law.

→ To know the equilibrium condition.

→ To know the spontaneity of the thermodynamic process.

→ To calculate the maximum fraction of heat can be converted to work.

Spontaneity is major basis of second law of thermodynamics.

Statement (kelvin and Clausius)

→ It is impossible to convert heat completely to an equivalent work without producing any change in the system or surrounding (Planck).

→ It is impossible for self acting machine unaided by external agency to convey heat from cold to hot body. (Clausius).

→ All natural and spontaneous processes take place in one direction & are thermodynamically irreversible.

* **Spontaneous or irreversible process :**

A spontaneus process is an irreversible process and may be reversed by an external agency. It is silent of rate of reaction.

e.g., Combination of hydrogen and oxygen is very very slow at room temperature but spontaneous.

Example : -Flowing of water from high attitute.

- Heat flows from hot end to cold end.

-Expansion gas high pressure to low pressure.

-Electricity flows from higher potential to a point of lower potential.

-Diffusion of solute from high concentration to low concentration.

-Flow of e^- from more electropositive metal (High oxidation potential) to less electropositive metal (Low oxidation potential or high reduction potential)

*** Decrease of enthalpy and spontaneity.**

As water falls due to change in potential energy. By analogy it can be told that a reaction occurs in the direction of decrease of energy i.e., $H_p < H_r$.

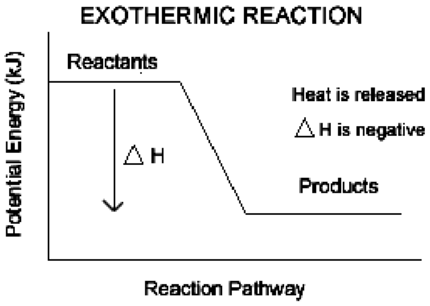
Example : Exothermic

$$\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightarrow NH_{3(g)} \qquad \Delta_r H = -46.1 kJ/mol$$

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O(\ell) \qquad \Delta_r H = -285.8 \text{ kJ/mol}$$

$$\Delta H = H_p - H_r = \text{negative } \left(H_r > H_p\right)$$

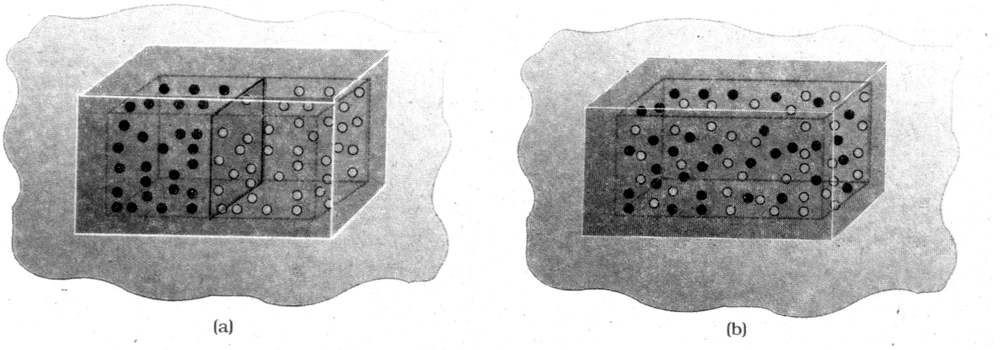
This shows the decreases in enthalpy (may) be the basis of spontancity of the process.



$\frac{1}{2}N_{2(g)} + O_{2(g)} \longrightarrow NO_{2(g)}$ $\Delta_r H = +33.2\,kJ/mol$ is endothermie but spontaneous. Thus decrease in enthalpy may be a contributory factor for spontancity, but it is not true all cases.

* **Entropy and spontaneity :**

Let us take another example where no change of enthalpy $(\Delta H = 0)$, diffiusion of gases.



→ Before mixing (i.e.,partion is there) A=black dots, B=white dots

From Left 'A'(g)molecules & from might (B) (g) molecules can surely be obtained.

→ After mixing (partition removal), we are not sure whether molecules picked up are gas (A) or gas (B) i.e., the system becomes less pedictable and more **chaotic.**

Now we may formulate another postulate that is an isolated system there is always a tendency for the systems energy to become more disordered or chaotic & this could be a criterion for spontaneity. Thus another thermodynamic function entropy (S) is introduced to measure the disorderedness or randomness of the system. Higher the randomness greater in the entropy e.g., solid has lower entropy while gas has higher entropy.

→ Entropy quantified : When heat (q) is added to the system, it increases molecular motion increasing the randomness in the system.

Thus, heat (q) has randomsing influence. Also temperature (T) is the measure of chaotic motion of particles in the system. Heat added at lower temperature causes greater randomness than when the same quantity of heat added to it at higher temperature This suggests that entropy change is inversely propertional to temperature. So, $\boxed{\Delta S = \frac{q_{rev}}{T}}$.

$q_{(rev)}$ is the quantity of heat absorbed by a reversible system (where change occurs infinitesimally small manner without distrubing the equilibrium in each change)

→ Unit of entropy : J K^{-1} mol^{-1}

Features of entropy :

(i) Greater is the randomness greater is the entropy.

(ii) Factors affecting change in entropy :

→ Physical state solid → liquid → Gas

[ΔS becomes increasingly positive]

→ Temperature - Increase of temperature increases entropy.

→ Decomposition of compound increases entropy.

$$CaCO_3(S) \longrightarrow CaO(S) + CO_2(g),\ \Delta S = +ve\ .$$

(iii) In an isolated system, for a spontaneous process ΔS should be positive i.e. $\Delta S > 0$.

(iv) For all pure crystals entropy is taken as zero i.e., no disorderedness.

(v) Like $\Delta H, \Delta U$ entropy is a state function as disorderedness depends on internal energy / heat content..

$$\Delta S = S_{firal} - S_{initial}$$

(vi) The total entropy change (ΔS_{total}) for all system and surroundings a spontaneous process is given by $\Delta S_{total} = (\Delta S_{system} + \Delta S_{surrounding}) > 0$

(vii) At equilibrium, $\Delta S = 0$

(viii) In a thermodynamically reversible process where equilibrium is maintained throughout, the entropy of the system and the surrounding taken together remains unchanged.

HOME ASSIGNMENT

(i) The unit of entropy is ____________ .

(ii) What is sign of ΔS for decomposition of $KClO_3$?

(iii) What is the value of ΔS when temperature falls to 0 K ?

(iv) For $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3$, the entropy change (ΔS) is –549.4 J K^{-} mol^{-1} at 298 K. Inspite negative entropy change why such reaction is spontaneous ? $\left[\Delta_r H \text{ for the reaction} = -1648 \times 10^3 J/mol.\right]$

(v) Which of the following is not a state function ?

(a) Temperature (b) pressure (c) entropy change (d) work

(vi) Write down the limitations of first law of thermodynamics.

(vii) What do you mean by thermodynamic reversibility ?

(viii) What happens to ΔH and ΔS for spontaneity ?

L-61. Gibbs energy and spontaneity :

As most of the chemical reaction follows open/closed system, there are changes in both enthalpy and entropy. Neither decrease of ΔH nor the increase of ΔS can satisfactorily explain the spontaneity of the reaction, so new thermodynamic function, Gibbs energy on Gibbs function G, defined as G = H – TS to explain the spontaneity / direction of the reaction. This is the driving force to explain whether the reaction is feasible or not. G is an extensive properly and a state function.

Thus, $G = H - TS$

differentiating both sides – $dG = dH - TdS - SdT$

At constant temperature, $dG = dH - TdS$

i.e, $\boxed{\Delta G^0 = \Delta H^0 - T\Delta S^0}$ at standard state.

→ Unit of $\Delta G = J/mol$

→ It is defined as the amount of energy available from a system that can be put into useful work.

→ ΔG and spontaneity :

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$$

If the system is in thermal equilibrium with surrounding then temperature is same as that of system.
The decrease in energy of the system (exothermic) = increase is enthalpy of the surrounding.

$$\text{i.e., } \Delta S_{surrounding} = \frac{-\Delta H_{system}}{T} = \frac{\Delta H_{surrounding}}{T}.$$

$$\Delta S_{total} = \Delta S_{system} + \left(\frac{-\Delta H_{system}}{T}\right)$$

Now $T\Delta S_{total} = T\Delta S_{system} - \Delta H_{system} = -\Delta G_{system}$

For spontaneous process $\Delta S_{total} > 0$

i.e., $-\Delta G_{system} > 0$, more is the spontaneously.

More in the –ve value of ΔG, $\left[\Delta G_{system} = \Delta H_{system} - T\Delta S_{system}\right]$

Decrease of free energy makes the reaction feasible.

L-62

* **Effect of temperature on spontaneity of reaction :**

$\Delta_r H^0$	$\Delta_r S^0$	$\Delta_r G^0$ $= \Delta H^0 - T\Delta S^0$	**Description**
–	+	–	Reaction spontaneous at all temperature
–	–	–	Reaction spontaneous at low temperature
–	–	+	Reaction non-spontaneous at high temperature
+	+	+	Non-spontaneous at low temperature
+	+	–	Spontaneous at high temperature TdS > ΔH

+ – – Non-spontaneous at all temperature.

[temperature to be regulated to make ΔG negative.

Consider a general reversible reaction :

$$A + B \rightleftharpoons C + D$$

At equilibrium $\Delta G = 0$

Remember :

$$\Delta G = \Delta G^0 + RT \ln K$$

ΔG^0 = standard free energy change when all reactants and products are at their standard state of unit activity (concentration)

K = thermodynamic equilibrium constant for above chemical reaction

$$0 = \Delta G^0 + RT \ln K$$

$$\Delta G^0 = -RT \ln K = -2.303\ RT \log K$$

$$\log K = -\frac{\Delta G^0}{2.303RT} = -\left[\frac{\Delta H^0 - T\Delta S^0}{2.303RT}\right]$$

For exothermic reaction, $\Delta H^0 = -ve$ and $\Delta S^0 = +ve$, log K value will be much larger than 1 at low temperature.

Higher the value of K better is the yield, the reaction proceeds in forward direction. This is in support of Le-chatelier's principle.

→ For endothermic reaction :

→ The over all tendency for a reaction to be spontaneous is to acquire a **state of minimum energy and maximum radonness.** This overall tadency is called, the **driving force,** calculated from **Gibbs - Helmhottz equation,** $\Delta G = \Delta H - T\Delta S$.

→ At high temperature entropy factor predominates where as at low temperature the energy factor predominates.

* Third law of thermodynamics :

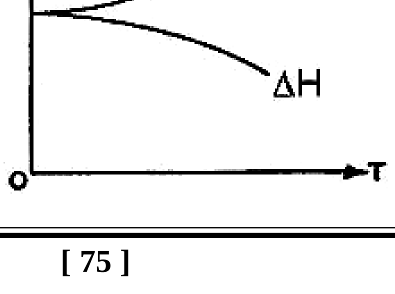
First law– Concept of energy contest of the system.

Second law – concept of entropy (measure of disorderedness) and direction of the reaction.

3rd law – (Nernst) limitation on the value of entropy of a crystalline solid. No new concept.

→ Nernst heat theorem : The value of ΔG and ΔH of system becomes equal to each other at absolute zero of temperature. (T = 0 K) and approach each other asymptotically.

Graphically :



Thus : $\left(\frac{\Delta G}{\partial T}\right)_P = \left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta C_P$

$\quad T \to 0 \qquad T \to 0$

We know $G = H - TS,$ $\qquad H = U + PV$

$dG = dH - TdS - SdT,$ $\qquad dH = dU + PdV + VdP$

$dG = d\cancel{U} + Pd\cancel{V} + VdP - T\cancel{d}S - SdT$

$\therefore$ From first law and entropy $TdS = dU + PdV$

i.e., $dG = VdP - SdT$

So $\left(\frac{\partial G}{\partial T}\right)_p = -S$ (or) $\left(\frac{\partial \Delta S}{\partial T}\right)_p = -\Delta S$

When $T \to O$, $\Delta S = 0$ i..e, $\boxed{\lim_{T\to 0} \Delta S = 0}$

→ **Definition of 3rd law :**

At absolute zero of temperature the entropy of every substance may become zero and it does become zero in case of perfectly crystaline solid.

HOME ASSIGNMENT

(a) The sign of enthalpy of neutralisation is _________ .

(b) The value of change of heat capacity of a substance at absolute zero is _________ .

(c) Mention the relationship between ΔG and the equilibrium constant.

(d) What happens to a reaction with $\Delta G, \Delta H$ and ΔS values positive and all negative?

(e) Evaporation of water is endothermic, but why is it spontaneous ?

(f) Can Al_2O_3 be reduced by Na metal at 298 K ?

$$\Delta G^0_{(Na_2O)} = -360,\ \Delta G^0_{(Al_2O_3)} = -1498\ \text{kJ/mol}$$

Remember $\Delta G^0_{(\text{element})} = 0$.

UNIT - VII
EQUILIBRIUM

L-63 :

Introduction :

Equilibrium represents the state of a process in which the properties like temperature, pressure, concentration of a system do not show any change with passage of time.

On this basis changes (physical & chemical) are of two types : reversible and irreversible. In the reversible process equilibrium is reached when the rates of the two opposing process become equal.

Physical change : $H_2O(\ell) \rightleftharpoons H_2O(\text{vap})$

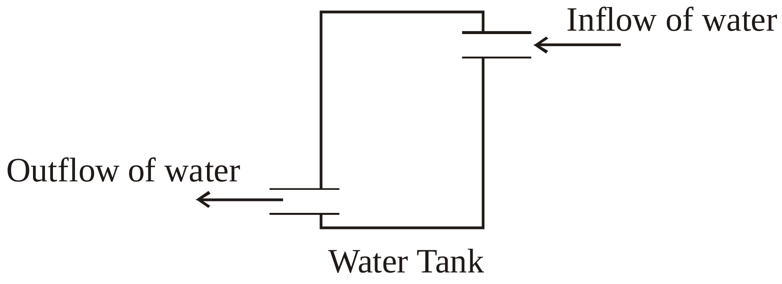
$\rightleftharpoons$ sign of reversibility

Chemical charge : $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

→ **Dynamic nature of equilibrium :**

Illustration :

(i)

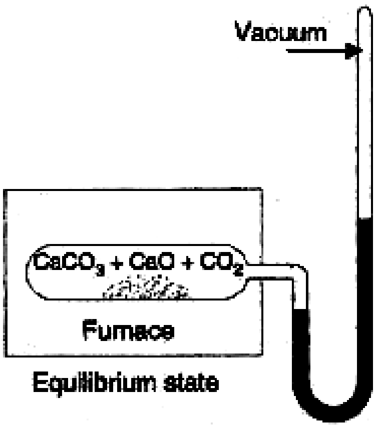


rate of inflow > rate of out flow, water level in the tank increases.
rate of inflow < rate of out flow, water level decreases
rate of inflow = rate of out flow equilibrium is reached water level remains fixed. No change with progress of time .

→ Inflow and out flow **never stops** i.e process is dynamic in nature. The effect on water level is not marked as two opposing rates are identical.

(ii) Decomposition of $CaCO_3(s)$

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_{2(g)}$$



At equilibrium the monometer reading i.e., mercury level remains fixed indicating rate of decomposition of $CaCO_3(s)$ is equal to rate of association of CaO and CO_2 i.e. the backward reaction.

(iii) **Draw Diagram :**

$$N_2O_{4(g)} \rightleftharpoons 2NO_2$$

Colourless reddish brown

Initially the reddish brown colour deepens indicating decomposition of N_2O_4 and then becomes constant i.e., an intermediate colour between colourless and deep reddish brown i.e., a faded colour at 25^0C. So long as the temperature remains same, the colour remains unchanged. This indicates the state of equilibrium where two opposing rates (forward and back ward) are identical but the two reactions never stops i.e. the process is dynamic.

Thus, knowledge of equilibrium approached _____

(i) Constancy of level i.e., pressure remains unchanged

(ii) Constancy of colour (Reactions where change in colour observed)

(iii) Constancy of concentration (composition)

$$A \rightleftharpoons B$$

Case I → concentration of A i.e., [A] is less i.e. point of equilibrium is towards right, [B] is muchmore

case II [A] is more

point equilibrium is towards left.

case III [A] = [B]

Point of equilibrium is reached. This shows the dynamic nature of equilibrium.

Thus, the extent of a reaction in equilibrium varies with experimental conditions such as concentration of reactants, temperature etc.

There fore, study of equilibrium predicts the extent of product to be obtained in a process.

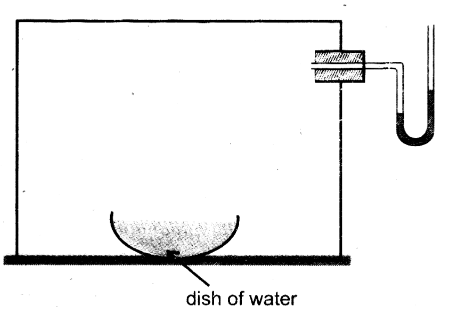
Equilibrium in physical process :

→ solid $\rightleftharpoons$ liquid

Example : Ice(s) $\rightleftharpoons$ water(ℓ)

Rate of melting of ice = rate of freezing of water. Equilibrium is maintained at freezing point when two states are having identical vapour pressure.

→ **Liquid vapour equilibrium.**



Equilibrium : rate of evaportion $\rightleftharpoons$ rate of condensation. V.p. increases and at a time it becomes constant indicating approach of equilibrium at a given temperature. The time taken for complete evaporation depends on –

(i) nature of the liquid (ii) amount of the liquid (iii) the temperature. In the open system no equilibrium is reached. At 1-bar pressure becomes 1 atm. pressure the equilibrium is maintained at its p.p. i.e. boiling point of liquid is the temparatureat which v.p. becomes 1-atom. Pressure attaining, liquid $\rightleftharpoons$ vapour. When pressure decreases the boiling point decreases.

→ **Solid- vapour equilibrium :**

Ex. $I_{2(solid)} \rightleftharpoons I_{2(vapour)}$ constancy of intensity of colour indicates approach of equilibrium.

→ **Solid in liquid :** (Dissolution of solid)

Sugar (solution) $\rightleftharpoons$ Sugar (solid)

Rate of dissolution of sugar = rate of crystallisation (Precipitation)

The solubility of the solid in the solution is constant at constant temperature.

Putting some radioactive sugar is solution the dynamic nature can be studied. Radioactive sugar can be formed in both the phases : solution phase (liquid) and precipitate (solid)

→ **Gas - solution equilibrium**

$CO_{2(g)} \rightleftharpoons CO_2$ (in solution) example. soda water.

At equilibrium $\frac{\text{conc. of gas is aqueous solution}}{\text{conc. of gas in gaseous phase}}$ = constant at a given temperature.

The amount of gas dissolved is goverened by **Henry's law :**

The mass of the gas dissolved in a given mass of a solvant at any temperature is directly proportional to pressure of the above the solvent i.e., $m \propto p$ or m = KP ehere K, the proportionality constant called Henry's constant.

HOME ASSIGNMENT

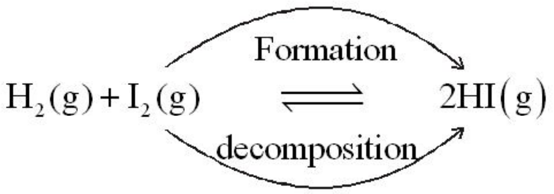
(a) What do you mean by dynamic nature of equilibrium ?
(b) How can you observe the equilibrium between water and its vapour ?
(c) Provide two examples of solid - vapour equilibrium.
(d) State Henry's law.
(e) For phase change when equilibrim is reached ?

L-64

Chemical Equilibrium :

It is defined as the state of system in which its properties do not change with time.

→ **Reversible reaction :** The reaction which can proceed from either side.



Equilibrium is reached when rate of formation is equal to rate of decomposition i.e., the $[H_2]$, $[I_2]$ and [HI] do not change with time at a given temperature.

→ Irreversible reaction : The reaction proceeds from reactant side only.

Example : Precipition reaction : $AgNO_3 + KCl \rightarrow AgCl + KNO_3$

Displacement reaction : $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

Decomposition reaction : $KClO_3 \rightarrow KCl + \frac{3}{2}O_2$

Such reaction tends to get completed but never undergoes equilibrium. The concentration of reactant(s) goes on decreasing.

* **Types of chemical equilibrium :**

(i) Homogeneous equilibrium - Reactants and products are in same phase.

Gaseous phase $N_{2_{(g)}} + 3H_{2_{(g)}} \rightleftharpoons 2NH_{3_{(g)}}$

Liquid phase

$$CH_3COOH(\ell) + C_2H_5OH(\ell) \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$$

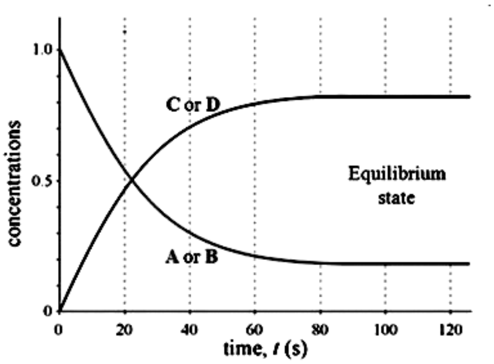
(ii) heterogeneous equilibrium. Reactants & products are is different phases.

$NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$ Two phases.

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_{2(g)}$ Three phases.

* Chemical equilibrium and rate of reaction

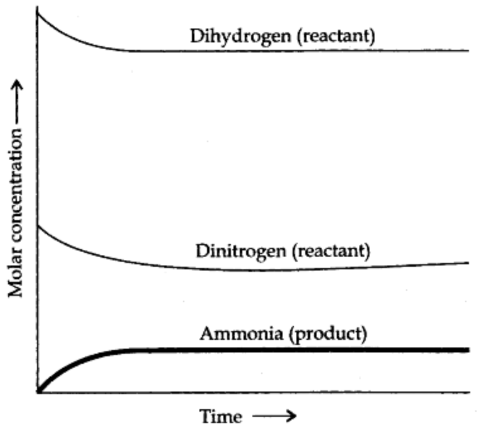
$$A + B \rightleftharpoons C + D$$



Attainment of chemical equilibrium

Equilibrium (constancy of composition of A, B, C and D after some time)
Graph showing Attainment of equilibrium :

Depiction of equilibrium for the reaction, $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$



Depiction of equilibrium for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

* **Characteristics of equilibrium : / Factors affecting equilibrium.**

→ The state of equilibrium is possible only when the equilibrium is carried in closed vessel (for reactions involving gases, homogeneous or heterogeneous equilibrium)

→ At equilibrium the property of the system like concentration (intensity of colour), temperature and pressure remain unchanged.

→ Since equilibrium can shift towards product or towards reactant, it's dynamic in nature.

→ State of equilibrium can be approached from either side.
→ At equilibrium both opposing rates are identical. ($r_f = r_b$).
→ Catalyst if added never affect the state of equilibrium.
→ Addition of inert gas also affect the state of some equilibrium.

HOME ASSIGNMENT

(a) How can you know the sugar(s) $\rightleftharpoons$ sugar (solution) equilibrium in reached?
(b) Why catalyst does not alter the state of equilibrium ?
(c) What happens to vapour pressure of water at equilibrium state ?
(d) Can a reversible reaction proceed to completion ?
(e) Identify two gases which are highly soluble in water ?

L-65. Law of mass action (Norwegian chemists, Goldberg - Waage)

Statement : Rate at which a substance reacts is propertional to its molar concentration (active mass) and the rate of chemical reaction is propertional to the product of the molar concentration of the reactants raised to the power equal to the stoichiometric coefficients.

$$A \longrightarrow \text{product}$$

rate of reaction $\propto [A]$

$$2A \longrightarrow \text{product}$$

$$A + A \longrightarrow \text{product}$$

rate of reaction $\propto [A]\,[A]$

$\propto [A]^2$ (Coefficient becomes the power of the concentration)

In ganeral :

$$aA + bB \longrightarrow \text{products}$$

According to the law of mass action,

rate of reaction $\propto [A]^a\,[B]^b$

$= k\,[A]^a[B]^b$

k is a proportionalilty constant called **rate constant.**

Application : Derivation of equilibrium constant, K

$$aA + bB \underset{k_2}{\overset{k_1}{\rightleftharpoons}} cC + dD$$

$k_1 =$ rate constant for forward

$k_2 =$ rate constant for backward reaction.

Now $r_f = K_1[A]^a\,[B]^b$, ${}^{r}_{3}b = k_2[C]^c\,[D]^d$

At equilibrium $r_f = r_b$

Now $\dfrac{k_1}{k_2} = K_c = \dfrac{[C]^c[D]^d}{[A]^a\,[B]^b}$

* Law of chemical equilibrium

Definition of K :

→ If it's a gaseous homogeneous equilibrium the active mass can be expressed in partial pressure form.

So $K_p = \dfrac{p_c^c\ p_D^d}{p_A^a\ p_B^b}$

→ If the active mass expressed in mole fraction form.

$$K_x = \frac{X_C^c . X_D^d}{X_A^a . X_B^b}$$

Relationship between K_p & K_C, $pV = nRT$

$$p = \frac{n}{v} RT, \quad P = CRT$$

$$p_A = [A]RT, \quad p_A^a = [A]^a [RT]^a$$

Now $K_p = k_c.(RT)^{\Delta n}$

We know p = mole fraction × total pressure, p = partial pressure

Derive $K_p = K_x.P^{\Delta n}$ $\qquad p_A = X_A P$

$$\Delta n = (c + d) - (a + b)$$

* Characteristics of equilibrium constant (K)

(i) It has a definite value for every reaction at a given temperature. However, it changes with temperature.

(ii) It does not depend on initial concentration / pressure / mole fraction but those at equilibrium state.

(iii) K value odoes not change with presence of catalyst, as catalyst affect the rate constants (k_1 and k_2) identically.

(iv) The equilibrium constant value is inversed if the equilibrium is reversed.

i.e., $H_2 + I_2 \rightleftharpoons 2HI$

$$K_1 = [HI]^2 / [H_2][I_2]$$

Equilibriumapproached from backward reaction :

$$2HI \rightleftharpoons H_2 + I_2$$

$$K_2 = \frac{[H_2][I_2]}{[HI]^2}$$

Now $K_1 = \dfrac{1}{K_2}$

(v) The value of K predicts the extent of reaction. Higher is the 'K' value greater is the product i.e., reaction proceeds more in forward direction.

(vi) Unit of K. Unit varies from one to another.

e.g. $H_2 + I_2 = 2HI$ $\qquad \Delta n = 0$

K_c or K_p or K_x has no unit

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \quad \Delta n = 1$$

K_c = mol/*l*

i.e. in general unit $K_c = (mol / L)^{\Delta n}$

HOME ASSIGNMENT

(a) Write the K_p expression for $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

(b) How does it relate to K_C ?

(c) What is the unit of K_C in moles / L ?

(d) 1 gram H_2 reacts with 2 gram of iodine. Calculate the mole fraction of H_2 in it.

(e) The equilibrium constant for $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is K, what will be the K'

for $\frac{1}{2}N_2(g) + \frac{3}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$

(f) Show that $K_p = K_x p^{\Delta n}$

L-66 Relation between K_p, K_C and K_x :

Now $\boxed{K_P = K_C.(RT)^{\Delta n} = K_X.P^{\Delta n}}$

For the equilibrium $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$, $\Delta n = 0$

So $K_P = K_C = K_X$

Reaction quotient and equilibrium constant :

Definition : For the reaction , aA + bB $\rightleftharpoons$ cC + dD

At any stage of reaction (not at equilibrium), the ratio, $\frac{[C]^s[D]^d}{[A]^a[B]^b}$ is termed as reaction quotient, Q_C

similarly of gaseas equilibrium $Q_p = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$

(i) If Q = K, the reaction is at **equilibrium.**

(ii) If Q > K, Q will tend to decrease to become equal to K i.e., the reaction will proceed is **backward direction.**

(iii) If Q < K, Q will tend to increase. As result the reaction will proceed in **forward** direction..

* Q and ΔG

$\Delta G = \Delta G^0 + RT \ln Q$ (at any stage of reaction At equilibrium, $\Delta G = 0$ and Q = K

$$0 = \Delta G^0 + RT \ln K$$

$$\boxed{-\Delta G^0 = RT \ln K}$$

* **Equilibrium constant and Temperature :**

With rise of temperature the rate of forward reaction and rate of back ward reaction change i.e., K_f and K_b (rate constants of two opposing reactions) value change differently with rise or fall in temperature. Since K=kf/K_b. changes with temperature. For endothermic **increases** ($k_f > k_b$) and K value for exothermic reaction decreases ($k_b > k_f$) with **rise** in temperature. Temperature does not affect a reaction for which $\Delta_r H = 0$.

Remember van't equation (integral form)

$$\log\frac{K_2}{K_1} = \frac{\Delta_r H^0}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

K_1 equilibrium constant at temperature T_1 .

K_2 equilibrium constant at temperature T_2

$\Delta_r H^0$ = standard enthalpy change of reaction

R = Gas constant, 8.314 J/mol/K

HOME ASSIGNMENT

(a) Show that $K_2 < K_1$ for exothermic reaction with rise of temperature i.e. the exothermic reaction proceeds in back ward direction with rise in temperature.

(b) Ice melts with rise is temperature - explain.

(c) In the formation of HI, the concentrations of H_2, I_2 and HI are found to be 0.5 mole, 0.4 mol and 3 mol respectively at equilibrium state at a given temperature. Calculate the K value What is the equilibrium constant if the decomposition equilibrium is studied at that temperature.

(d) For above process, $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ at an arbitary stage the concentrations are found to be ,H_2, 0.25 mol, I_2, 0.3 mol and HI, 2 mole at that temperature. Find out direction of the progress of reaction. K = 50 (given)

(e) $PCl_{5(g)}$ decomposes 80% to attain equilibrium at a given temperature. Calculate its K_C and K_P at 1 atmospheric pressure.

(f) Find at the $\frac{K_P}{K_C}$ value for the following gaseous equilibria.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

$$2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$$

L-67

Factors affecting the state of equilibrium -

Le-chatelier's principle.

Statement : If a system in equilibrium is subjected to external stres, such as concentration, temperature, pressure, introduction of inactive gas etc the equilibrium shifts in the direction of reaction which tends to undo or nullify or reduce the effect of that stress.

→ **Effect of concentration :**

The concentration stress of an added reactant / product is releived by net reaction in the direction that the added substance.

addition of oxidate to reduce Fe^{3+}.

Expt. $Fe^{3+}_{(aq)} + SC\bar{N}_{(aq)} \rightleftharpoons [Fe(SCN)]^{2+}_{aq}$

yellow colourless deep red

Case-I Reduction of $[Fe^{3+}]$ on adding oxalic acid when equilibrium is reached i.e., attaining constancy of colour. To releive the stress the dissociation of $[Fe(SCN)]^{2+}$ takes place to replenish the Fe^{3+} i..e, the equilibrium shifts in backward direction. This can be known as the intensity of red colour decreases.

Case II Addition KSCN increases [SCN] & the intensity of red colour increases indicating the equilibrium shifts to right.

$$K_C = \frac{\downarrow\left[Fe(SCN)\right]^{2+}_{(aq)}}{\downarrow\left[Fe^{3+}\right]\left[SC\bar{N}_{(aq)}\right]}$$

The decrease of concentration of Fe^{3+} decreases the dr. value as K_C is constant at a given temperature, the nr. must have to decrease proportionately i.e. equilibrium shifts towards left.

→ **Effect of temperature :**

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -57.2\,kJ/mol$$

brown colourless

$$\xleftarrow{\text{increase of temperature at equilibrium.}}$$

Expt.

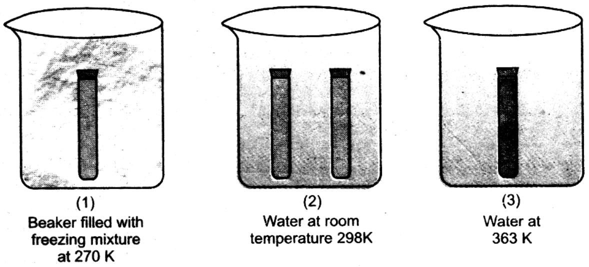


Fig. *Effect of temperature on equilibrium for the reaction,* $2NO_2$ (g) *f* N_2O_4 (g)

Quantitatively :

$$\log\frac{K_2}{K_1} = \frac{\Delta_r H}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

For exothermic reaction, $\Delta_r H = -ve$

$T_2 - T_1 = +ve$ i.e. increase of temperature.

$$\log \frac{K_2}{K_1} = -ve$$

i.e., K_2 is **less**. That is at higher temperature the product decreases indicating the equilibrium shifts towards **left.**

→ **Effect of pressure :** With increase of pressure (or decrease of volume by compression) the reaction proceeds is a direction of decrease of volume $\left(P \propto \frac{1}{V}\right)$ at a given temperature.

Case I $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2(O)_{(g)}$ $\Delta n = -ve$ i.e. 2-4 = -2 mole

$$\xrightarrow{\text{increase of external pressure}}$$

Case II $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ $\Delta n = +ve$

$$\xleftarrow{\text{increase of external pressure}}$$

Case III $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ $\Delta n = 0$

Presure has no effect on the state of equilibrium.

HOME ASSIGNMENT

(a) Predect the effect of temperature and pressure on the following equilibria -

(i) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 92.38\ \text{kJ/mol}$

(ii) $\text{Ice(s)} + Q\ \text{kJ} \rightleftharpoons \text{water (vapour)}$

(b) What are the factors affecting equilibrium ?

(c) What happens to $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$, if carried out in a hot water both ?

(d) Identify two examples of equilibrium which are not affected by external presssure.

(e) Show that decomposition of PCl_5 if the volume of the contained is increased.

L-68 Quantitative approach to pressure effect :

Exp - $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ $\Delta n = +ve$

$$\xleftarrow{\text{increase of pressure}}$$

Initial	a	0	0
moles at equil	a-x	x	x
partial pressure	$\frac{a-x}{a+x}P$	$\frac{x}{a+x}P$	$\frac{x}{a+x}P$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{x^2p^2}{(a+x)^2} / \frac{a-x}{(a+x)}.P = \frac{x^2p}{a^2-x^2}$$

Thus, x^2P = constant P = applied pressure.

$x \propto \frac{1}{\sqrt{p}}$ i.e. with increase of pressure the quantity of PCl_5 decomposed (x) decreases & Equilibrium shifts towards left.

→ **Effect of a catalyst :** Catalyst does not affect the equilibrium composition of a reaction mixture.Catalyst does not appear in the balanced chemical equation or in the K expression.

→ **Effect of inert gas addition :**

* At constant volume of inert gas (Ar) is added (at equilibrium state) which does not take part is the reaction, the equilibrium remains undisturbed as it does not change the partial pressure or concentration of the reactants / products.

* **At constant pressure :** If inert gas introduced at constant pressure and temperature the increase in no of moles increases the volume i.e., the reaction proceeds in the direction of increase of volume. The gaseous reactions with Δn positive favours with introduction of inert gas.

* **Applications** of Lechatelier's principle

→ Synthesis of NH_3 by Haber's process :

(i) Effect of concentraion : High concentration N_2 and H_2 in pure and dry state.

(ii) Effect of temperature : $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)} + 92.38\,kJ/mol$

Exothermic. Hence optimum temperature of around 500^0C just to have the reaction kinetically feasible.

(iii) Effect of pressure : $\xrightarrow{\text{Increase of pressure (200 atm)}}$

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)} \quad \Delta n = -ve$$

(iv) Catalyst : Finely divided iron in presence of Mo or Al_2O_3 promoter.

→ Manufacture of H_2SO_4 by contact process :

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H = -192.5\,kJ$$

(i) Conc : high concentrations of pure and dry SO_2 and O_2.

(ii) Temperature As exothermic, an optimum temperature of around 450^0C, needed to start the reaction.

(iii) Pressure - Around 2 atom pressure (1.5 - 1.7 atm)

(iv) catalyst V_2O_5.

→ Manufacture of nitric oxide -

$$N_{2_{(g)}} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \qquad \Delta H = +179.1\,kJ/mol$$

- High temperature as process is endothermic
- Pressure has no effect as $\Delta n = 0$

- High concentration of $N_{2(g)}$ and $O_2(g)$, pure and dry.

→ Manufacture of HNO_3 (Ostwald process)

$$NH_{3(g)} + \frac{5}{4}O_{2(g)} \longrightarrow NO_{(g)} + \frac{3}{2}H_2O_{(g)}$$

i.e. $4NH_{3(g)} + 5O_{2(g)} \longrightarrow 4\,NO_{(g)} + 6\,H_2O_{(g)}$ $\Delta H = -905.2\ kJ/mol$

- Catalyst Pt with 10% Rh
- (moderate) temperature
- low presure
- high concentration of reactants

HOME ASSIGNMENT

(a) Calculate the equilibrium constant for the reaction

$$CO_{2(g)} + H_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)} \text{ at 1359 K,}$$

if the equilibrium constant at this temperature for the following are

$$2H_2O \rightleftharpoons 2H_{2(g)} + O_{2(g)}, \qquad K_1 = 2.1\times10$$

$$2CO_{2(g)} \rightleftharpoons 2CO + O_2, \qquad K_2 = 1.4\times10$$

(b) What are the conditions for better yield of ammonia by Habber's process ?

(c) Correct the following statements if it's found incorrect keeping the underlined intact.

(i) Nitric acid is synthised by contact process.

(ii) Introduction of Ar favours better yield of ammonia.

(iii) Decomposition $CaCO_3(s)$ is an exampale of hetergeneous equilibrium.

(iv) Combustion of C (s) at equilibrium favourably is affected by increase of pressure.

(d) Match the following :

	[A]		[B]
1.	Vanadium pentoxide	6.	Dalton's law
2.	Aluminium oxide	7.	Contact process
3.	Platinum	8.	Formation of HI
4.	$K_p = K_c$	9.	Moderate
5.	Partial pressure	10.	Oxidation of NH_3
		11.	Promotor

L-69. Ionic equilibrium : On the basis of conductivity Faraday classification the presence of two types of substance : electrolyte and non electrolyte. Electrolytes are those which conduct electricity either in solution or in molten state. In both the cases they dissociate into ions. These are again of two types : **strong** electrolyte and weak electrolyte. Strong electrolytes (salts) completely dissociate when dissolved.

They also present as ions in solid state. In solid they can't conduct electricity as the ions are strongly held by stronger force of attraction.

In weak electrolyte the molecules are partly ionised hence there exists an equilibrium between molecular state and ionised state. This is approached when the rate of dissociation into ions equal to rate of association into molecules.

e.g., $CH_3COOH(Aq) \rightleftharpoons CH_3COO(Aq) + H^+(Aq)$

H^+ (Aq) may be written a H_3O^+. Such an equilibrium is called **ionic equilibrium.**

$$K = \frac{[CH_3COO(Aq)][H^+(Aq)]}{[CH_3COOH]}$$

* Acid and bases

(a) Arrhenius theory of acids.

→ acids can provide H^+ ions in aqueous solution. e.g. HCl

→ Bases can provide OH^- ions in aqueous solution. e.g. KOH

→ Neutralision of acid-base to form salts is due to

$$\underset{(acid)}{H^+} + \underset{(base)}{OH^-} \longrightarrow H_2O(\ell)$$

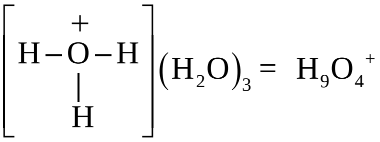
→ Due to electrolysis of acid, $H_2(g)$ at anode.

At cathode $H^+(aq) + e^- \rightarrow \frac{1}{2}H_{2(g)} \uparrow$

At anode $4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$

→ **Limitation :**

(i) $H^+(Aq)$ exists as H_3O^+ (pyramidal), hydronium ion. Which on further hydration by H-bonding to form $H_9O_4^+$.



$$\left[\begin{matrix} \overset{+}{\text{H}-\text{O}-\text{H}} \\ \quad | \\ \text{H} \end{matrix}\right](H_2O)_3 = H_9O_4^+$$

(ii) Substances without H^+ or OH^- can behave as acid and base e.g CO_2 (acidic), NH_3(basic)

$$\underset{\text{Base}}{2NaOH} + \underset{\text{acid}}{CO_2} \longrightarrow \underset{\text{Salt}}{Na_2CO_3} + H_2O$$

$$\underset{\text{Base}}{NH_3} + \underset{\text{acid}}{HCl} \longrightarrow \underset{\text{Salt}}{NH_4Cl}$$

(b) Bronsted - Lowry acids and bases : (Proton transfer theory)

Acid – proton donor

Base – proton acceptor

acid base pair ($+H^+$)

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{conj acid}}{H_3O^+} + \underset{\text{conj base}}{Cl^-}$$

Conj. acid-base pair ($-H^+$)

Acid – H^+ = conj. base

Base + H^+ = conj acid

→ **Features of this theory :**

(i) Acid base pairs that differ only by one proton are called conjugate acid base pairs.

Cl^- is the conjugate base HCl (acid)

(ii) Not only molecules but also ions can act as acid and base.

Acid / molecule CH_3COOH, HCl, HNO_3 (proton donors)
Acid \ ions NH_4^+, H_3O^+, $NH_4^+ \longrightarrow NH_3 + H^+$
$H_3O^+ \longrightarrow H_2O + H^+$

Base / molecules NaOH, NH_4OH
Base \ ions (all anions) HCO_3^- $(HCO_3 + H^+ \rightarrow H_2CO_3)$
$CO_3^= + H^+ \longrightarrow HCO_3^-$

(iii) The conjugate base of a stronger acid is weaker & vice versa.

$$\underset{\text{(strong acid)}}{HClO_4} \longrightarrow \underset{\text{weak base (conj.)}}{ClO_4^- + H^+}$$

$$\underset{\text{(weak acid)}}{CH_3COOH} \longrightarrow \underset{\text{Strong base (conj.)}}{CH_3COO^- + H^+}$$

(iv) All Arrhenius acids are Bronsted acid but Bronsted acids are not Arrhenious acids e.g. NH_4^+ is not as Arrhenius acid. CO_3^{2-} is not a base per Arrhenins, but it's is Bronsted base. $CO_3^= + H^+ \longrightarrow HCO_3^-$

(v) Neutralisation reaction takes place when acid base reaction takes place in equivalent amounts.

(vi) Acid only behaves acidic is a basic medium & vice versa.

e.g. HCl behaves acidic is water (base) but not in benzene (not a proton acceptor).

(vii) The equilibrium constant values (Ka or K_b) helps to compare the strength and predict weaker & strongeracids. Amphoteric nature of H_2O can be explained.

Limitations : Fails to explain the acidic character of CO_2, SO_2, AlF_3, BF_3... and basic character of ZnO, CaO etc.

(c) Lewis theory : Acid - electron acceptor
Base - electron donor

→ **Lewis acid :**

(i) simple cations, Cu^{++}, Ag^+, Ca^{2+}
(ii) (electron deficient species). BF_3, $AlCl_3$, $ZnCl_2$, $FeCl_2$.........
(iii) Molecules with multiple bands CO_2, SO_2, SO_3 etc.
greater the s-character greater the acidic nature.
(iv) Molecules with vacant d-orbitals. $SiCl_4$, SiF_4

$$\underset{\text{acid}}{SiF_4} + \underset{\text{Base}}{2F^-} \longrightarrow [FiF_6]^{2-}$$

→ **Lewis bases :**

(i) All simple anions : CN^-, Cl^-, OH^-

(ii) Molecules with excess pair of e^-(s), $\ddot{O}H_2$, $\ddot{N}H_3$,

$R\ddot{N}H_2$, $R\underset{\cdot\cdot}{\ddot{O}}H$, $R-\underset{\cdot\cdot}{\ddot{O}}-R$

$$R\ddot{N}H_2 + H^+ \longrightarrow R\overset{+}{N}H_3$$

electron doner

→ **Acid-Base reaction (Lewis)**

$$F_3B + :NH_3 \longrightarrow F_3B \longleftarrow :NH_3$$

electron deficient

→ **Limitations :**

(i) Relative strength can't be predicted as it does not undergo ionisation.
(ii) Acid-base reactions are slow due to formation of dative bond.
(iii) Catalytic property of acids can't be explained by Lewis theory.
(iv) It can't explain the <u>amphoteric nature</u> of H_2O, HCO_3^- ions etc.

HOME ASSIGNMENT

(a) Identify acids from the following and name these as Arrhenius / Lewis / Bronsted.

HCl, Cl^-, HCO_3^-, SO_4^{2-}, BCl_3, $SiCl_4$, H_2O, N^+H_4, ClO_4^-

(b) How do Lewis acids differ from Bronsted acids ?
(c) $CH\equiv CH$ behaves acidic in $NH_3(l)$ but not in water, why ?
(d) $CH\equiv CH$ is acidic, reacts with $NaNH_2$ but not with NaOH, Why ?

L-70

Ionisation of acids and bases :

Comparison of strength and study of equilibrium

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

acid base conj acid conj. base

This is a dynamic equilibrium involving transfer of proton in forward and reverse direction. Let us consider two acids : HA and H_3O^+ & to study which one is stronger proton donor. The equilibrium shifts in the direction of weaker acid. The stronger acid donates proton to stronges base.

Applying law of equilibrium to above. –

$$K_C = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$[H_2O]$ = constant, as it is present in excess.

$$K_C[H_2O] = \frac{[H_3O^+][A^-]}{[HA]} = Ka$$ (disociation constant of acid)

It is constant at a given temperature.

If the original conc of HA c mol/L and $'\alpha'$ degree of ionisation/ dissociation. At equilibrium '$C\alpha$' dissociates.

i.e., $[HA] = C - C\alpha,\ [H_3O^+] = [A^-] = C\alpha$

Substituting respective value –

$$Ka = \frac{C\alpha.\cancel{C}\alpha}{\cancel{C}(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

If 'α' is very small in comparison to 1.0.

$$Ka \simeq C\alpha^2 \qquad \alpha = \sqrt{\frac{Ka}{C}}$$

i.e, on dilution or decrease of concentration of the solution the degree of ionisation (α) increases as 'α' protortional to $\alpha \frac{1}{\sqrt{C}}$

This is called **Ostwald dilution law.**

At some concentration, 'C', two acids with ionisation constant $Ka_{(1)}$ & $K_{a(2)}$ will be

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a(1)}}{K_{a(2)}}} = \frac{\text{strength acid(1)}}{\text{Strength acid (2)}}$$

Thus one can compare the strength of acids if Ka values are known.

Simillar for K_b i.e, dissociation constant of base can be explained.

Ionisation of polybasic acid :

Basicity : The no. of moles of base (OH^-) that can completely neutralise 1 mole of acid in dilute solution.

$HCl + OH^- \longrightarrow H_2O + Cl^-$ mono basic acid / monoprotic

$H_2SO_4 + 2OH^- \longrightarrow 2H_2O + SO_4^{2-}$ Dibasic acid.

$H_3PO_4 + 3OH^- \longrightarrow 3H_2O + PO_4^{3-}$ Tribasic acid.

(3. moles of base)

$H_nA + n\,(OH)^- \longrightarrow n\,H_2O + A^-$ Polybasic acid.

Let us consider a diprotic acid, H_2X (aq) which ionises in two steps :-

$$H_2X_{(aq)} \rightleftharpoons H^+_{(aq)} + HX^-$$

Strong acid weak acid,

$$K_1 = \frac{[H^+][HX^-]}{[H_2X]}$$

$$HX^-_{(aq)} \rightleftharpoons H^+_{(aq)} + X^- \qquad K_2 = \frac{[H^+][X^-]}{[HX]^-}$$

Anino

K_1 and K_2 are 1st and 2nd ionisation constant of acid H_2X. This dissociation constants of poly basic acid gradually decrease i.e. subsequently weaker acids are formed. Proton donating decreases because proton containing aninos are formed.

HOME ASSIGNMENT

(a) Compare the basic strength of ClO_4^{1-}, ClO_3^-, ClO_2^-, ClO^-, Cl^-

(b) Explain the following :

- (i) H_2CO_3 is a stronger acid than HCO_3^-.
- (ii) HCO_3^- can act acid and base.
- (iii) H_2O is an amphoter.
- (iv) $(CH_3)_2NH$ is more basic than CH_3NH_2.
- (v) Phosphoric acid is tribasic acid.
- (vi) Percentage of ionisation of an weak electrolyte increases on dilution.
- (vii) Show that $K_a \times K_b = K_w$.

L-71

Factors affecting acidic strength :

(i) Bond strength : weaker the bond strength H–A, stronger is the acid.

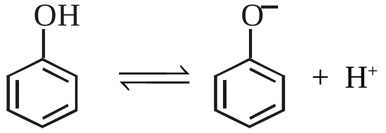
$$H - I > H - Br > H - Cl > HF$$

(ii) With increase of electro-vity of A, the polarity of H–A bond increases increasing acidic strength.

$CH_4 < NH_3 < H_2O < H–F$

Electronegativity F > 0 > N > C

(iii) Stability of the conjugate base :



Conjugate base phenoxide ion is stablised by resonance. More stable is the conjugate base more is the acidic nature.

Nitrophenol in more acidic than phenol.

(iv) – I effect : $Cl–CH_2COOH > CH_3COOH$

(v) Increase in positive O.N. of the same element.

$$\mathrm{H\overset{+7}{Cl}O_4 > H\overset{+5}{Cl}O_3 > H\overset{+3}{Cl}O_2 > H\overset{+1}{Cl}O > H\overset{-1}{Cl}}$$

$$\mathrm{H\overset{+7}{Cl}O_4 > H\overset{+7}{B}\ O_4 > H\ \overset{+7}{I}\ O_4}$$

In case of same O.N., greater is the electro-vity greater is the acidic behaviour.

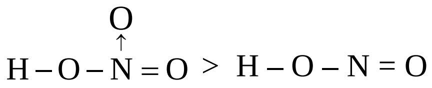
(vi) Multiple bond formation : Greater is the s.character greater is the $\overline{e}$ - accepting tendency, hence more acidic nature.

$$CH \equiv CH > CH_2 = CH > CH_3 - CH_3$$

$$sp \quad\quad sp^2 \quad\quad\quad sp^3$$

s-character. 50%   33.3%   25%

(vii) Presence of more unprotonated 'O' (oxygen)



$$H-O-\overset{\overset{O}{\uparrow}}{N}=O > H-O-N=O$$

Unprotonated 'O' = 2   = 1

(viii) Ka value : Higher is the Ka value or less is PKa value more is the acidic nature.

* **Ionisation constant of water & its ionic product (k_w) :** Water both acts proton donor and proton accepter i.e.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

Applying law of equilibrium $K = \dfrac{\left[H_3O^+\right]\left[OH^-\right]}{\left[H_2O\right]^2}$

$\left[H_2O\right]$ almost remains content.

Now $\boxed{K_w = \left[H_3O^+\right]\left[OH^-\right]}$, ionic product of water.

Definition : Ionic product of water is the mathematical product of under concentration of hydronium and hydroacid ions at a given temperature.

At 25^0C its experimentally found to be 1.0×10^{-14} M^2. Its it value depends on temperature, at 100^0C $K_w = 75 \times 10^{-14}\, M^2$

$$\text{Molarity of water} = \frac{1000}{18} = 55.55\,M$$

Thus, $\dfrac{\text{dissociated part}}{\text{undissociated part}} = \dfrac{10^{-7}}{55.55} = 1.8 \times 10^{-9}$ i.e. the equilibrium lies mainly towards undissociated water (left).

For pure water $\left[H_3O^+\right] = \left[OH^-\right] = 10^{-7}$ moles / L

Acidic $\left[H_3O^+\right] > \left[OH^-\right]$

Basic $\left[H_3O^+\right] < \left[OH^-\right]$

$$\left[OH^-\right] = \frac{K_w}{\left[H_3O^+\right]}$$

* pH and pH scale :

P = Puissanced hydrogen (French word) i.e. power of Hydrogen. pH is defined as the negative logarithm of activity of H^+ (aH^+) in a solution at a given temperature i.e., $pH = -\log aH^+$

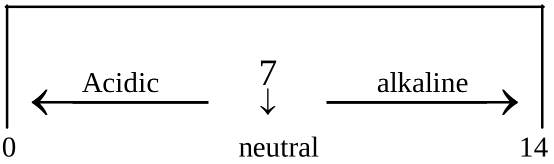
$$\mathrm{pH} = \log \frac{1}{\left[\mathrm{H}^{+}\right]} = -\log\left[\mathrm{H_3O}^{+}\right]$$

$$\mathrm{K_w} = \left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right] = 10^{-14}$$

$$-\log \mathrm{K_w} = -\log\,[\mathrm{H}^{+}] - \log\,[\mathrm{OH}^{-}] = +14$$

$$\boxed{\mathrm{PK_w} = \mathrm{pH} + \mathrm{pOH} = 14}$$

pH scale :



When $[\mathrm{H}^{+}]$ changes by a factor 100, the value of changes by 2 units

$\left[\mathrm{H}^{+}\right] = 10^{-2}\,\mathrm{M}$ $\qquad$ $\left[\mathrm{H}^{+}\right] = 10^{-2} \times 10^{-2} = 10^{-4}$

pH = 2 $\qquad$ pH = 4 (Solution 100 times diluted)

Calculation of pH of different solutions.

Short problems : (Refer text)

HOME ASSIGNMENT

(a) Calculate the pH of following solutions :

- (i) 2 gram NaOH dissolved is 500 ml solution.
- (ii) 0.365 gram HCl present 200 ml solution
- (iii) 0.04 M HCl and 0.04M H_2SO_4 solution.

(b) Calculate the mass of NaOH present in 200 ml solution of pH 8.

(c) 100 ml of 0.5 M HCl is added to 400 ml 0.2 $NHNO_3$.
Calculate the pH of the resulting solution.

(d) 100 ml of 0.2 N NaOH is mixed with 100 ml of 0.1N HCl. Calculate pH of the resulting solution.

(e) 2 grams of NaOH dissolved is 1L solution. Calculate $[\mathrm{H}^{+}]$ is it.

(f) Calculate the pH of 10^{-8} M solution of HCl.

L-72 BUFFER SLON :

Statement : It is a solution, whose pH value does not change appreciably by addition of a small amount of either acid or alkali from outside i.e. buffer solution preserves its pH value.

→ **Types of buffer :** (a) simple buffer (b) Mixed buffer

Simple buffer : Salts of weak acid & weak base

e.g. NH_4CN, CH_3COONH_4

Mixed buffer : (i) acidic buffer - solution containing weak acid and its salt (conjugate base) e.g. one mole CH_3COOH + one mole of CH_3COONa (CH_3COO^-) having pH < 7 (4.75).

(ii) Basic buffer - equimolar mixture of weak base & its salt (Conjugate base)

One mole of NH_4OH + one mole of NH_4Cl (NH_4^+), pH>7 (9.25)

→ **Buffer action :** pH of the buffer solution almost remains unchanged on addition of acid or alkali.

(i) **Simple buffer** $CH_3CO\bar{O}\overset{+}{N}H_4$ ·

$$CH_3CO\bar{O} + \overset{+}{N}H_4 \begin{cases} \xrightarrow{H^+ \text{added}} CH_3CO\bar{O}(aq) + H^+(aq) \rightarrow CH_3COOH(aq) \\ \xrightarrow{O\bar{H}\ \text{added}} NH_4^+ + O\bar{H} \rightarrow NH_4OH(\text{weak base}) \end{cases}$$

On adding few drops of acid (H^+) or alkali (OH^-) weak acids, CH_3COOH or weak base, NH_4OH are formed respectively.

The formation of these in the solution never changes the pH appreciably as these are weak with less K_a and K_b values.

(ii) **Acidic buffer :**

$$\underbrace{\begin{matrix} CH_3COOH + CH_3CO\bar{O} \\ HA + A^- \end{matrix}} \begin{cases} \text{Drops } H^+ \text{ (acid) added } CH_3CO\bar{O} + H^+ \longrightarrow \underset{\text{weak acid}}{CH_3COOH} \\ \text{drops of } OH^- \text{ (alkali added from outside)} \\ CH_3COOH + OH^- \longrightarrow \underbrace{CH_3COO^- + H_2O}_{\text{Never affect pH}} \end{cases}$$

(iii) Basic buffer, $\underbrace{NH_4OH + NH_4^+}_{\text{solution}}$ –

$$\begin{cases} \text{Drops of } H^+ \text{ (acid) added } NH_4OH + H^+ \longrightarrow \underbrace{\underset{\text{weak acid}}{NH_4^+ + H_2O}}_{\text{Never affect pH}} \\ \text{drops of } OH^- \text{ (base/alkali) added} \\ NH_4^+ + OH^- \longrightarrow NH_4OH(\text{weak base}) \\ \text{Never increases pH value appreciably} \end{cases}$$

* Calculation of pH of buffer solution

(i) Acidic buffer $\underset{\text{(Weak acid)}}{HA} \rightleftharpoons H^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$\Rightarrow \quad [H^+] = K_a \times \frac{[HA]}{[A^-]} \quad \Rightarrow -\log[H^+] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

$$\mathrm{pH} = \mathrm{pK_a} + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

i..e, $\boxed{\mathrm{pH} = \mathrm{pK_a} + \log\frac{[\mathrm{salt}]}{\mathrm{acid}}}$

[A] = mostly the concentration of salt

[HA] = conc^n o f weak acid never dissociates much to increase the conc^n of [A$^-$] or decrease the conc^n [HA]

This is called Henderson - Hasselbalch equation or simply Henderson equation.

For equimolar solution i.e. [Salt] = [acid]

$\mathrm{pH} = \mathrm{pK_a}$

For alkaline buffer, Henderson's equatio will be -

Derive → $\mathrm{POH} = \mathrm{pK_b} + \log\frac{[\mathrm{Salt}]}{[\mathrm{Base}]}$

$$\mathrm{pH} = 14 - \mathrm{pOH} = 14 - \mathrm{pK_b} - \log\frac{[\mathrm{Salt}]}{[\mathrm{Base}]}$$

→ **Applications :**

- * In qualitative and quantitative analysis.
- * Industrial process such as manufacture of paper, dyes, inks ....
- * In Agriculture, medicine etc.

Types of salt : → **General classification :**

(a) Simple salt –

(i) Normal salt, NaCl

(ii) Acid salt $NaHSO_4$ Partial neutralisation of poly basic acid.

$$\mathrm{NaHSO_4 + NaOH \longrightarrow \underset{\text{normal salt}}{Na_2SO_4} + H_2O}$$

(iii) Basic salt (to react with acid forming normal salt)

$$\underset{\text{Basic salt}}{\mathrm{BiOCl}} + 2\mathrm{HCl} \rightarrow \underset{\text{Normal salt}}{\mathrm{BiCl_3}} + \mathrm{H_2O}$$

(b) Complex salt . $K_4[Fe(CN)_6]$

Fe^{2+} and CN^- lose their identity.

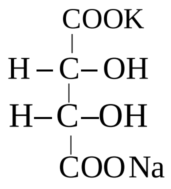
(c) Double salt. $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$ Potash alum

$(NH_4)_2 SO_4.FeSO_4.6H_2O$ (Mohr. salt)

(d) Mixed salt $Na(NH_4)HPO_4$ – micro cosmic salt.

Replacement of H^+ by different cation of poly basic acid.

Rochelle salt.



$$\begin{array}{c}\mathrm{COOK}\\ |\\ \mathrm{H-C-OH}\\ |\\ \mathrm{H-C-OH}\\ |\\ \mathrm{COONa}\end{array}$$

(Sodium potassium tartarate)

→ **Classification on the basic of hydrolysis :**

(i) Salts of strong acid strong base, K_2SO_4

(ii) Salts of strong acid and weak base, NH_4Cl

(iii) Salts of weak acid and strong base, CH_3COONa

(iv) Salts weak acid & weak base, CH_3COONH_4

HOME ASSIGNMENT

(a) Solution of ammonium acetate acts a buffer solution - explain.

(b) Why aqueous solution of NaCl does not act as a buffer solution ?

(c) Discuss buffer action of an acidic buffer.

(d) How can you calculate the pH of an alkaline buffer ?

(e) Calculate the pH of a solution obtained by mixing 5 ml of 0.1M with 250 ml of 0.1 NH_4Cl solution. K_b for $NH_4OH = 1.8 \times 10^{-5}$.

L 73. Hydrolysis salt : It is a chemical reaction where the cation / anion part of the salt interact with water. rendering the solution acidic or alkaline.

(i) The salts of strong acid and strong base on hydrolysis makes the solution **neutral**. pH remains unchanged i.e., pH = 7 (of water) Such salt, do not undergo hydrolysis.

(ii) Salts of strong acid and weak base : e.g. NH_4Cl

$$NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

i..e, on hydrolysis of cation part of the salt the solution becomes acidic. As acid e.g. **s** stronger $\left[H^+\right] > \left[OH^-\right]$.pH < 7 **.**

$$\boxed{pH = 7 - \frac{1}{2}\left(pK_b + \log C\right)}$$

K_b = dissociation constant of weak base.

(iii) Salts of weak acid and strong base : e.g. CH_3COONa

$$CH_3CO\bar{O} + Na^+ + H_2O \rightleftharpoons Na^+ + OH^- + CH_3COOH$$

$$CH_3CO\bar{O} + H_2O \rightleftharpoons CH_3COOH + OH^-$$

Thus, hydrolysis of anion part of the salt renders the solution alkaline pH > 7.

$$K_n \text{ (hydrolysis constant)} = \frac{\left[CH_3COOH\right]\left[OH^-\right]}{\left[CH_3COO^-\right]}$$

$$= \frac{\left[CH_3COOH\right]\left[O\bar{H}\right]\left[H^+\right]}{\left[CH_3COO^-\right]\left[H^+\right]} = \frac{K_w}{K_a}$$

$$K_a = \frac{\left[CH_3COO^-\right]\left[H^+\right]}{\left[CH_3COOH\right]}$$

$$K_w = \left[H^+\right]\left[OH^-\right]$$

*
$$\begin{array}{cccc} CH_3COO^- + H_2O & \rightleftharpoons & CH_3COOH & + OH^- \\ C & & O & O \\ C(1-h) & & Ch & Ch \end{array}$$

h = degree of hydrolysis

$$K_h = \frac{Ch \times Ch}{C(1-h)} = \frac{Ch^2}{(1-h)}$$

$$K_h \simeq Ch^2 \qquad h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a \times C}}$$

→ **Calculate of pH of solution :**

$$\left[OH^-\right] = Ch$$

$$= C \times \sqrt{\frac{K_w}{K_a \times C}} = \sqrt{\frac{K_w \times C}{K_a}}$$

$$-\log[OH^-] = -\frac{1}{2}\log K_w + \frac{1}{2}\text{Log}\, K_a - \frac{1}{2}\log C$$

$$pOH = 7 + \frac{1}{2}\log K_a + \frac{1}{2}\log C$$

$$\because \; K_w = 10^{-14}$$
$$-\log K_w = +14$$

$$pH = 14 - 7 - \frac{1}{2}\log K_a + \frac{1}{2}\log C$$

$$-\frac{1}{2}\log K_w = 7$$

$$\boxed{pH = 7 + \frac{1}{2}\left(pK_a + \log C\right)}$$

i.e.,pH > 7 (hence alkaline)

→ **Salts of weak acid and weak base.**

Let us take the example of $CH_3\,COONH_4$.

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons NH_4OH + CH_3COOH$$

Here both cation and anion part of the salt get hydrolysed.

The nature of the solution depends on K_a of the acid & K_b of the base.

If $K_a = K_b$, the solution is almost neutral
$K_a > K_b$, the solution is acidic
$K_b > K_a$, the solution is alkaline.

→ hydrolysis constant, K_h

$$K_h = \frac{[NH_4OH][CH_3COOH]}{\left[CH_3CO\bar{O}\right]\left[NH_4^+\right]}\frac{\left[H^+\right]\left[OH^-\right]}{\left[H^+\right]\left[OH^+\right]} = \frac{K_w}{K_a.K_b}$$

$$K_a = \frac{\left[CH_3COO^-\right]\left[H^+\right]}{[CH_3COOH]},\ K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{[NH_4OH]},\ K_w = \left[H^+\right]\left[OH^-\right]$$

→ Degree of hydrolysis (h)
Initial molarity at equillibrium

$$\begin{array}{ccccccc} CH_3COO^- & + & NH_4^+ & + H_2O \rightleftharpoons & NH_4OH & + & CH_3COOH \\ C & & C & & O & & O \\ C(1-h) & & C(1-h) & & Ch & & Ch \end{array}$$

$$K_h = \frac{Ch.Ch}{C(1-h).C(1-h)} = \frac{h^2}{(1-h)^2}$$

Now $\quad K_h \simeq h^2$

$$h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a.K_b}}$$

→ pH of the solution

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{\left[CH_3COO^-\right]\left[H^+\right]}{[CH_3COOH]}$$

$$\left[H^+\right] = K_a\frac{[CH_3COOH]}{CH_3COO^-} = K_a.\frac{Ch}{C(1-h)} = K_a.\frac{h}{1-h}$$

$$= K_a\,.\,h \qquad \because 1-h \text{ taken as } 1.$$

$$= K_a \times \sqrt{\frac{K_w}{K_a.K_b}}$$

$$= \sqrt{\frac{K_w.K_a}{K_b}}$$

$$\log [H^+] = \frac{1}{2}\log K_w + \frac{1}{2}\log K_a - \frac{1}{2}\log K_b, -\log [H^+]$$

$$= -\frac{1}{2}\log K_w - \frac{1}{2}\log K_a + \frac{1}{2}\log K_b$$

$$\boxed{pH = 7 + \frac{1}{2}\left(\log K_b - \log K_a\right)} = 7\frac{1}{2}\left(pK_a - pK_b\right)$$

$K_a = K_b$, $\quad pH = 7 \quad$ neutral

$K_a > K_b$, $pH < 7$ acidic

$K_b > K_a$, $pH > 7$ alkaline

Here ammonium acetate solution is almost neutral, as $K_a \simeq K_b$

* Derivation is given for clear understanding.

HOME ASSIGNMENT

(a) Predict the nature of following salts is aqueous solution. ammonium sulfate, sodium carbonate, ammonium cyanide, benzene diazonium chloride, Anilinium bisulfate, methyl amine hydro chloride, Tetramethyl ammonium sulfate. Potassium sulfate, Calcium nitrate ammonium nitrate.

(b) Calculate the pH of 0.01M solution of NH_4CN. Ka for HCN = 6.2×10^{-10} and K_b for $NH_3 = 1.6 \times 10^{-5}$.

(c) Account for the following :

- (i) NaCl (Aq) is neutral while $NH_4Cl(aq)$ is acidic.
- (ii) pH of ammonium acetate solution is independent of its concentration.
- (iii) Ions of the salt get hydrolysed.
- (iv) The term hydrolysis differs from hydration.

L 74

* **Solubility Product :** It is defined as the mathematical product of the molar concentrations of its ions raised to the power equal to the number of times each ion occur in the equation representing dissociation of the salt at a given temperature.

In case of sparingly soluble salt there exists equilibrium between soluble part (ions) and isoluble part (s) is molecular state.

e.g.
$$\underset{\text{undissociated}}{AgCl(s)} \rightleftharpoons \underbrace{Ag^+(aq) + Cl^-(aq)}_{\text{Solution (ions)}}$$

Applying low of equilibrium

$$K = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

$$K[A_gCl] = [Ag^+][Cl^-]$$

$$\Rightarrow \quad K_{S_p} = [Ag^+][Cl^-] \qquad [AgCl(s)] = \text{constant}$$

In general – $M_xA_g(s) \rightleftharpoons x\ M^{y+} + yA^{x-}$

$$\boxed{K_{S_p} = [M^{y+}]^x [A^{x-}]^y}$$

→ Solubility product and solubility (moles/L)

Let ‘s’ moles necessary to make a saturated solution of 1L.

$$M_x^-A_y(s) \rightleftharpoons xM^{y+} + yA^{x-}$$

$$\qquad\qquad xs \qquad ys$$

$$K_{S_p} = [xs]^x (ys)^y$$

$$= x^x\, y^y\ \ s^{x+y}$$

Solubility $s = \left(\dfrac{K_{SP}}{x^x y^y}\right)^{1/x+y}$

e.g. solubility of AgCl = s = $\sqrt{\left(K_{S_p}\right)}$

$$K_{S_p} = s^2$$

Higher is the K_{S_p} greater is the solubility.

→ Ionic product, Q_{SP} and solubility product, K_{SP}

$$\text{For } M_xA_g \rightleftharpoons x\ M^{y+} + y\,A^{x-}$$

$Q_{SP} = [M^{y+}]^x[A^{x-}]^y$ (concentrations not at equilibrium)

case (i) $Q_{SP} = K_{SP}$, the solution is just saturated and no precipitation takes plac.

(ii) $Q_{SP} > K_{SP}$, the solution is saturated and **precipitation takes place**.

(iii) $Q_{SP} < K_P$, the solution is unsaturated, no precipitation.

Applications : (i) Knowledge of precipitation

(ii) From K_{SP} values the solubility of different salts canbe compared.

(iii) Qualitative analysis : cations can be classified in groups depending on K_{SP} values.

e.g. Ag^+, Hg_2^{++}, Pb^{2+} are included in group - I as they precipitate as chloride. There chlorids are insoluble as these have very low K_{SP} values.

e.g. CuCl (K_{SP} = 1.7 × 10^{-6}), $H_{g_2}Cl_2\left(K_{S_p}\right) = 1.3\times10^{-18}$.

(iv) Separations of solids by the process of **fractional crystallisation,** the solid (salt) with less K_{S_p} value crystallisse faster.

* **Common ion effect :** Let us study the dissociation of NH_4OH (weak base) in presence of $NH_4Cl\left(NH_4^+\right)$.

$$\overset{\longleftarrow}{}$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$

Here N^+H_4 is common to both & the dissociation is supressed.

$$K=\frac{\uparrow\left[NH_4^+\right]\left[OH^-\right]}{\uparrow\left[NH_4OH\right]}$$, Increase Conc^n of N^+H_4 increases the Nr-value

as K_b is a constant Conc of $\left[NH_4OH\right]$ must have to increase proportionately i.e, the equilibrium shifts towards left. pH decreases.

Thus, the presence of common ion supresses the ionisation of a weak electrolyte.

Application :

(i) Solubility of spaingly soluble salt decreases in presence common ion

(ii) Salt can be separated from saline water on passing dry $HCl_{(g)}$ through it where Cl^- acts as a common ion. Increasing concentration of Cl^- helps to exceed its K_{SP} value and separates out.

$$\left[Na^+\right]\left[Cl^-\right]>K_{S_P}\,(NaCl)$$

$HCl_{(g)}$ is passed as its highly soluble and $[Cl^-]$ increases as volume of the solution never changes on passing $HCl_{(g)}$.

(iii) Salting out effect : Soap can be settled out on adding saturated solution of NaCl.

$$\overset{\xleftarrow{\hspace{3cm}}}{C_{17}H_{35}COO^-N_a^+ \rightleftharpoons C_{17}H_{35}COO^- + Na^+}$$

Soap (Stearate)

$$NaCl(aq)\longrightarrow Na^+ + Cl^-$$, Here Na^+ acts as common ion.

Common effect suppresses the dissociation.

(iv) Qualitative analysis :

Example :

(i) Precipitation group II radicals $(Pb^{2+},\ Hg^{2+},\ Cu^{++},\ Cd^{++}.........)$ on passage of $H_2S_{(g)}$ in presence of dil. HCl. Ion acidic medium (H^+ common ion) the $[S^{2-}]$ is reduced.

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$HCl_{(aq)}\longrightarrow H^+ + Cl^-$$

$$\left[Cu^{++}\right]\left[S^{2-}\right]>K_{SP}\left(C_us\right)$$

Measurable concentration $S^=$ helps to precipitate sulfids of Group II but not sulfides of group III, IV etc; which have higher K_{SP} values.

(ii) Precipitation of Group III_A Fe^{3+}, Al^{3+} and Cr^{3+} radicals as hydroxides. Reagent : NH_4Cl and NH_4OH. Due to common ion $\left(NH_4^+\right)$ concentration of OH^- is reduced and helps to exceed the lower K_{SP} values of hydroxides of Fe^{3+}, Al^{3+} and Cr^{3+}.

Group III_B $\left[Zn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}\right]$ as sulfides and Group IV $\left[Ba^{2+}, Sr^{2+}, Ca^{2+}\right]$ radical, as carbonates also obtained. It is explained in the light of common ion effect and K_{SP} values.

HOME ASSIGNMENT

(a) Give reason :

(i) Cu^{++} gets precipitated as sulphide in acidic medium while Zn^{++} in alkaline medium on passage of $H_2S_{(g)}$.

(ii) To precipitate Group II radicals $H_2S_{(g)}$ is passed in pressure HCl but not HNO_3 and H_2SO_4.

(iii) pH of NH_4OH is reduced in presence of NH_4Cl is solution.

(iv) Solubility AgCl is reduced in pressure of KCl.

(v) Weak acid dissociates more in presence of alkali.

(b) How to get sodium chloride from sea water without evaporating it ?

(c) When an ion gets precipitated ? Explain with example.

(d) What is the maximum concentration of equimolar solution of ferrous sulfate and sodium sulfide so that when mixed in equal volumes there is no precipitation of iron sulfide ?

$$K_{SP}\left(FeS\right) = 6.3\times10^{-18}.$$

UNIT - VIII

L-75, 76, 77, 78, 79

OXIDATION AND REDUCTION

Oxidation Reaction :

There are six different ways to know whether a chemical reaction is oxidation or not. They are:

1. Addition of oxygen is oxidation reaction

$$2Ca + O_2 \xrightarrow[\Delta]{} 2CaO$$

2. Removal of hydrogen is oxidationreaction.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

3. Addition of any electrongative elements (ENE / non metals) is oxidation reaction.

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$

4. Removal of any electropositive element (EPE / metals) is oxidation reaction.

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

5. Increase in the proportion of oxygen or any electronegative elements is an oxidation reaction.

$$\begin{array}{ccc} 2Cu_2O + O_2 & \longrightarrow & 4CuO \\ Cu : O & & Cu : O \end{array}$$

$$1:\frac{1}{2} \qquad\qquad 1:1$$

$$2\,CuCl + Cl_2 \longrightarrow 2\,CuCl_2$$

$$\begin{array}{cc} Cu : Cl & Cu : Cl \\ 1 : 1 & 1 : 2 \end{array}$$

6. Decrease in the proportion of hydrogen or any electropositive elements is an oxidation reaction.

$$SnCl_2 + Cl_2 \longrightarrow SnCl_4$$

$$\begin{array}{cc} Sn : Cl & Sn : Cl \\ 1 : 2 & 1 : 4 \\ \text{(or) } \frac{1}{2}:1 & \text{(or) } \frac{1}{4}:1 \end{array}$$

Reduction Reaction :

Reserve of oxidation is reduction. If we replace the word addition by the word removal or vice versa and replace the word increase by the word decrease or vice versa the above mentioned reaction for oxidation becomes reduction.

The easier way to decide whether a chemical reaction is oxidation or reduction is by calculation of oxidation number or oxidation state.

Oxidation Number (O.N.)

“ Oxidation number or oxidation state of an element (per atom) is the **amount of charge** developes over it while it either combines with itself or with some other elements (s). It may be +ve, –ve, Zero, fraction and may also varies from its compound to compound (s).

Rules to calculate oxidation Number.

1. Oxidation number of an element in its elementary state is zero.

Examples :

(i) O.N. of Na in sodium metal is zero. $\left(Na^0\right)$

(ii) O.N. of Fe in iron metal is zero $\left(Fe^0\right)$

(iii) O.N. of nitrogen in nitrogen molecule is zero. $\left(\underline{N}_2^0\right)$

2. O.N. of a compound as a whole is also zero.

Example :

(i) O.N. of KCl as a whole is zero

(ii) O.N. of $KMnO_4$ as a whole is zero.

3. O.N. of a metal is +ve and is uusally equals to its valency.

Example :

O.N. of potassium in KCl is +1.

$K^{+1}\ Cl^{-}$.

4. O.N. of a nonmetal is –ve and is usually equals to its valency.

Example :

O.N. of chlorine in KCl is –1.

$K\ \underline{Cl}^{-1}$

($\because$ O. N. of a compound as a whole is zero).

5. O.N. of hydrogen in all its compound is +1 except in metal hydrides where it is -1.

Example : In sodium hydride , NaH

$1 + x = 0$

$\because \; x = -1$

6. Oxidation number of oxygen in all its compound is –2, except in peroxides where it is –1,

Example : In Na_2O_2,

$2(+1) + 2x = 0$

$\therefore \; x = -1$

Oxidation and Reduction from O.N. point of view.

Oxidation : Oxidation is a process in which O.N. of an element (per atom) increases or in other words, there is removal of or more electrons.

Reduction : Reduction is a process in which oxidation number of an element (per atom) decreases or in other words there is addition of are more electrons.

Q. Why oxidation and Reduction akes place semultaneously ?

Ans. During oxidation process, there is removal of one or more electrons and during reduction process, there is addition of one more electrons. since during a chemical reaction, net change in number of electrons is zero, there fore oxidation and reduction reaction takes place simultaneously and hence known as **redox** reaction.

Oxidising agent is one which it self gets reduced.

Reducing agent is one which itself get, oxidised.

Balancing Redox reactions.

(a) By oxidation number method steps for balancing by O.N. method.

1. Calculate the O.N. of all the elements of reactants and products.
2. Find the change in O.N. of atoms which are oxidised and which are reduced.
3. Find the total change in O.N. of reducing agent and oxidising agent.
4. Write the total change in O.N. of reducingagent as a coefficient of oxidising agent and total change in O.N. of oxidising agent as a coefficient of reducing agent.
5. Balance the equation by hit and trial method.

Example :

$$FeCl_3 + SnCl_2 \longrightarrow FeCl_2 + SnCl_4$$

$$\begin{array}{ll|ll}
Fe \rightarrow +3 & & Fe \rightarrow +2 & \text{Change} \quad (1\times1=1) \\
Cl \rightarrow -1 & & Cl \rightarrow -1 & \\
Sn \rightarrow +2 & & Sn \rightarrow +4 & \text{Change} \quad (2\times1=2)
\end{array}$$

$$2\,FeCl_3 + SnCl_2 \rightarrow FeCl_2 + SnCl_4$$

$$2\,FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

By Hit and trial method.

(b) Balancing Redox reaction by ion - electron method.

Diferent steps are :

1. Separate oxidation step(know as oxidation half reaction) and reduction step (know as reduction half reaction).

2. Balance the atoms where O.N.is changed (By hit abd trial method) other than for ‘H’ and ‘O’.
3. Count the excess number of oxygen atom on each half reaction and balance by writing H_2O.
4. Count the excess number of Hydrogen atom an each half reaction and balance by writing H^+.
5. Add/remove electrons according to O.N.
6. Write two half reactions are below the other and cross multiply to cancell the electrons.

Examples :

$$MnO_4^- + Fe^{+2} + H^+ \longrightarrow Mn^{+2} + Fe^{+3} + H_2O$$

1. $MnO_4^- \longrightarrow Mn^{+2}$ $\qquad$ $Fe^{+2} \longrightarrow Fe^{+3}$

2. $MnO_4^- \longrightarrow Mn^{+2}$ $\qquad$ $Fe^{+2} \longrightarrow Fe^{+3}$

(since Mn is balanced) (since Fe is balanced)

3. $MnO_4^- \longrightarrow Mn^{+2} + 4H_2O$ $\qquad$ (since Fe is balanced)

4. $MnO_4^- + 8H^+ \longrightarrow Mn^{+2} + 4H_2O$ $\qquad$ (since Fe is balanced)

5. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$ $\qquad$ $Fe^{+2} - e^- \longrightarrow Fe^{+3}$

6.
$$\begin{array}{l} MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O \\ \underline{\quad Fe^{+2} - e^- \longrightarrow Fe^{+3} \quad] \times 5} \end{array}$$

$$MnO_4^- + 8H^+ + 5\ Fe^{+2} \longrightarrow Mn^{+2} + 4H_2O + 5Fe^{+3}$$

HOME ASSIGNMENT

1. Balance the following by oxidation number and ion lectron method :

$$H^+ + NO_3^+ + I_2 \longrightarrow IO_3^- + NO_2 + H_2O$$

$$MnO_4^- + H^+ + H_2S \longrightarrow M_n^{2+} + S + H_2O$$

$$Cr_2O_7^= + H^+ + CH_3 - CH_2OH \longrightarrow CH_3CHO + Cr^{3+} + H_2O$$

$$Cu + H^+ + SO_4^{2-} \longrightarrow Cu^{++} + SO_2 + H_2O$$

2. Name the products formed on oxidation of the following :

$HCOOH$, $H_2C_2O_7$, $S_2O_3^=$, I_2, $FeSO_4$, SO_2, SO_3^{2-}, H_2O_2, $Na_2S_2O_3$

3. Show that $KMnO_4$ is better used in acidic medium.
4. What is a disproportionate reaction ?
5. Mohr’s salt is used as a primary standard to standardise $KMnO_4$, why ?

L.80

Unit - IX

HYDROGEN (Henry Cavendish - 1766)

Position Hydrogen in Mandeleef periodic table is controversial de to following reasons.

i) **Resemblance with alkalimetals:**

(a) Identical valence shell configuration.

(b) electropositive character

$$HCl \longrightarrow H^+ + Cl^-$$

$$NaCl \longrightarrow Na^+ + Cl^-$$

(c) Oxidation state (I) $\overset{+}{H}Cl^-, Na^+Cl^-, C_s^+Cl^-$

(d) Combination with nonmetals -

Oxide	H_2O,	N_2O,	K_2O	....
Halide	HCl,	NaCl,	KCl	....
Sulfide	H_2S,	N_2S,	K_2S	....

(e) Discharged at cathode

$$H^+ + e^- \longrightarrow \frac{1}{2}H_2$$

$Na^+ + e \longrightarrow Na$ (metal) from fused NaCl

(f) Reducing character-

$$Fe_3O_4 + 4H_2 \xrightarrow[\Delta]{} 3Fe + 4H_2O$$

$$B_2O_3 + 6K \longrightarrow 2B + 3K_2O$$

(ii) **Resemblance with halogen-**

(a) Electronic configuration - one electron short of duplet.octet.
(stable configuration of noble gas)

(b) Electronegative character - $H + e^- = H^-$ (hydride)
$X + e^- \rightarrow X^-$ (halide)

(c) ΔiH, comparable with halogens but higher than alkalimetals.

(d)

	Li	H	F
ΔiH (kJ/mol)	520	1312.0	1681

(e) Liberation at anode on electrolysicphysics (e.g. electrolysis NaH(*l*).

(f) Atomicity (diatomic) H_2, X_2

(g) Combination with metal- $Na + \frac{1}{2}H_2 \rightarrow NaH$, $Na + \frac{1}{2}Cl_2 \rightarrow NaCl$

(h) Nonmetalic nature H(nonmetal) H (nonemetal)
Li (metal) F (non-metal)

(i) Formation of covalent bond CH_4 CCl_4

(j) Replecement of Hydrogen by halogen CH_4 CH_3Cl

(iii) **Difference from alkali metal & halogen-**

(a) Hydrogen can both act as oxidant and reductant $(H - e \rightarrow H^+)$ but alkalimetal reducing agent, halogens oxidant.

(b) Hydrogen has one electron (no neutron) but alkalimetals & halogens are polyelectronic and also contain more number of neutrons.

(c) In the molecular state hydrogen has two (nuclear) isomers o–H_2 and p–H_2.

(d) Nature of oxids -

	Li/Na/K	$\boxed{H}$	Cl/Br/I
	Basic (Li_2O)	Neutral (H_2O)	Acidic (Cl_2O_7)

(e) Absence of lone pair of electron $H:H$, $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$

(f) Nature of Compounds

(Ionic Compound) LiF , HF (covalent compound)

(iv) $\dfrac{\text{Thomson's Position in periodic table}}{\text{(Above carbon)}}$ $\underline{\text{Li Be B}}\ \overset{\overset{H}{\uparrow}}{C}\ \text{N O F}$

Similarity with Carbon :-

1. Half filled outer orbital

$$\overset{H}{1s^1\left(\frac{2}{2}\right)} \qquad \overset{C}{1s^2\ 2s^2\ 2p^2\left(\frac{8}{2}\right)}$$

2. Electro negativity - comparable H=2.1, C=2.5

3. Formation of covalent compound. $H-(HCl)$

$C-(CCl_4)$

* Occurrance : 70% of total mass of universe.

9th element in order of abundance

It is not found in the atmosphere due to absence of gravitational force (Lightest element/ molecule)

→ In the sum hydrogen fusion takes place give huge quantity of energy.

$$4\,{}_1^1H \longrightarrow {}_2^4He + 2\,{}_1^0e + \text{Energy}$$

Protium Helium (Position)

* **isotopes of hydrogen -**

	Protium ${}_1^1H$	Deuterium $\left({}_1^2H\right)$	Tritium $\left({}_1^3H\right)^*$
No of neutron -	0	1	2
Occurance - (%)	99.9844	0.0156 (in the form HD mostly)	in traces (one in 10^{18} parts)
Atomic mass (relative)	1.007825	2.014102	3.016049
Nuclear spin	$\frac{1}{2}$	1	$\frac{1}{2}$
Stability	Non-radioactive	Non-radioactive	Radioactive(*)

$${}_7^{14}N + {}_0^1n \rightarrow {}_6^{12}C + {}_1^3H$$

$${}_1^3T \longrightarrow {}_2^3He + {}_{-1}^0e$$

* **Nascent (newly born) hydrogen, H.**

It is more reactive than dihydrogen. It is formed in situ but evolved out H_2. When $H_{2(g)}$ in passed through electric are at 2000-3000^{0}C nascent H is formed at Low pressure. $H_2 \longrightarrow H + H - 433\,kJ$

$$KMnO_4 + H_2SO_4 + H_2 \longrightarrow \text{No reaction}$$

$$2KMnO_4 + 3H_2SO_4 + 10H \xrightarrow{Zn(H_2SO_4\,(dil))} K_2SO_4 + 2MnSO_4 + H_2O$$

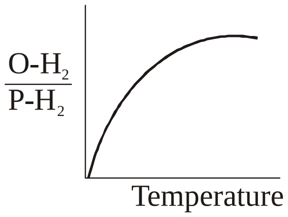
$$\underset{\text{Yellow}}{FeCl_3} + H \xrightarrow{Zn+H_2SO_4} \underset{\text{Light green}}{FeCl_2 + HCl}$$

* **Ortho and p-hydrogen :**

o-H_2 Same direction nuclear spin (spinning of proton)
p-H_2 antiparallel direction of nuclear spin.

Ordinary hydrogen (H_2) = 75% o–H_2 + 25% p-H_2 at normal temperature.

Temperature effect :



pure - p-H_2 can be prepared by adsorbing ordinary hydrogen in activated charcoal in quartez vessel kept at a temperature of 20K for 3 to 4 - hours. Pure o-H_2 has not so far been prepared.

These two hydrogen have different physical properties but have same chamical properties.

DIHYDROGEN

Preparation

$Zn\,(\text{granualated}) + HCl \longrightarrow$

$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$

Electrolysis of water $\longrightarrow H_2$ (Pt) cathode

$\underset{\text{Alkane}}{CnH_{2n+2}} + \underset{\text{(Steam)}}{nH_2O} \xrightarrow{Ni} nCO + (2n+1)H_2(g)$

synthesis gas / water gas

Properties

$H_2 + X_2 \longrightarrow 2HX$ (HFprepared even in dark)

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O, \Delta_f H = -285.09\,kJ/mol$

$H_2(g) + \frac{1}{3}N_2(g) \xrightarrow[673K,\,200atm]{Fe\,Mo} \frac{2}{3}NH_3\ \Delta_f H = -92.6\,kJ$

$H_2 + 2M \longrightarrow 3MH(s)$

M = alkalimetal (ionic compound)

with metal oxide (It is reduced to metal)

$YH_2(g) + M_xO_y(s) \longrightarrow x\,M_{(s)} + 3\,H_2O$

Vegetable oil + $H_2 \xrightarrow{Ni}$ vanaspati ghee

* Uses
(i) Starting national to prepare NH_3 by Haber's process.
(ii) Hydrogenation oil
(iii) Preparation of Fuel cell.
(iv) Manufacture of metal hydride.

Home Assignment

(a) The position of hydrogen in periodic table is controversial - explain.

(b) What are nuclear isomers of hydrogen ?

(c) Why pure zinc is not used to prapare $H_2(g)$?

(d) Conc. H_2SO_4 fails to liberate H_2 from zinc ?

(e) (i) What is water gas ? (ii) Show that 'H' both acts oxidant and reductant.

L-81 * **Hydrides :**

Almost all elements of periodic table (except noble gases and elements groups 7 (Mn - group), 8 (Fe group), 9 (Co-group) react with the dihydrogen under suitable conditions forming 'hydrides' with general formula MH_x. Three types : Ionic hydride, covalent hydride and metallic hydride.

→ Ionic hydride- group 1 and 2 except Be and Mg (Covalent polymeric hydride).

e.g. NaH, CaH_2(hydrolith)...

Properties -

(i) Hard wih high melting point.

(ii) Conduct electricity in molten state liberating to H_2 at anode.

(iii) density is higher than metal itself.

(iv) on hydrolysis liberates hydrogen.

$$CaH_2+2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

(v) $LiAlH_4$, $LiBH_4$ (complexes) used as reducing agent in organic synthesis.

→ Covalent or molecular hydride : p-block elements, Be, Mg form these hydrides with formula MH_{8-n} (n = no. of valence electron) These are suffixed by-ane when named.

e.g. PH_3 phosphane (cormonly phosphine)

OH_2 Oxidane (water)

NH_3 azane (ammonia)

These are of three types :

→ electron dificient hydride NH_3, AlH_3 (gr. 13)

→ electron-precise hydride CH_4, SiH_4 (gr. 14)

→ electron rich hydride : NH_3, :OH_2 (gr. 15, 16, 17)

→ Metallic or Non-stoichiometric or interstitial hydride.

The metals present in d-block and f-block except metals of group 7, 8 and 9 usually form metallic hydride. These hydrides are non-stoichiometric e.g. $LaH_{2.87}$, Yb $H_{2.55}$. The metals of group 7-9 which don't form hydrides, is refereed to as hydride gap. Hydrogen being smaller in size occupies some of the interstitial sites in the metallic lattice to form called interstitial hydride. Hydride lattice differ from the metal itself.

→ **Properties :**

(i) These are hard have metallic lusture, conducting electricity and have magnetic properties.

(ii) Density of hydrides lower than those of metals as the crystallattice expands due to inclusion of hydrogen.

(iii) The ratio of H atoms/ metal atoms for these hydride is not fixed to the metal is not fixed but varies with temperature and pressure.

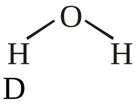
* Uses : In these, metals adsorb hydrogen on their surface. This property of adsorption of gas is called **occlusion.** The amound of $H_2(g)$ adsorbed on the surface follows in the order :

Collidal Pd > Palladiun > Platinum > gold > Nickel.

* **Water :**

Water is the most important natural source. It is essential to all forms of life but distribution of water over the earth's surface is not uniform. Oceans are the major source of water (Saline) 97.3% fresh water is less than 2.7 % (glaciers, ground water, rivers, lakes etc.) In nature it's present in all there phases: [(Ice(s), water(l), water vapour(g)

→ Structure of water and its aggregates :



sp^3 - hybridised dipolemorunt = 1.84

Shape bent O – H bond length = 95.7 pm

bond angle 104.5^0

Water (l) consists of aggregates of varying number of water molecules held together by H-bonding and free water molecules in a dynamic equilibrium with the aggregates continually forming - collasping & reforming. Ice exhibits Cage structure consequently the density of ice (s) is less than that water (l). The density of water is maximum at 277 K (4^0C).

→ **Physical and properties of water :**

(i) The freesing point, b.p., heat of fusion, $\Delta_{vap}.H$ are abnormally higher than those of hydrides of other elements of its group(16) due to pressence of H-bonding.

(ii) It has a higher specific heat, thermal conductivity and surface tension than most other liquids.

(iii) It has high dielectric constant (78.39) & used as better solvent (Aqueous solvent) for most of the ionic solids & covalent compounds exhibiting H-bonding with water. It is regarded as a universal solvent.

(iv) Heavy water (oxide of deutrium - D_2O) has slightly higher value of physical constants because of higher molecular mass (20.0276)

e.g. B.P. (water) = 373 K, B.P. (D_2O) = 374.4.

→ **Chemical properties :** Its reactivity can be accounted for its tendency to act as an acid, a base, an oxidant, a reductant and as a liquid in complexes.

→ Amphoteric nature -

$$H_2O + NH_3 \longrightarrow NH_4^+ + OH^+$$

Acid Base

$$H_2O + H_2S \longrightarrow H_3O^+ + HS^-$$

Base Acid

→ Redox reactions :

H_2O (oxidant)

$$H_2O + Na \longrightarrow NaOH_{(aq)} + \frac{1}{2}H_2(g)$$

H_2O (reductant)

$$2F_{2(g)} + 2H_2O \longrightarrow O_2(g) + 4H^+(aq) + 4F^-(aq)$$

In photosynthesis water gets oxidised to oxygen.

$$6\ CO_2(g) + 12\ H_2O(l) \longrightarrow C_6H_{12}O_6(aq) + 6H_2O + 6O_2(g)$$

→ Hydrolytic reaction :

$$CaO + H_2O(l) \longrightarrow Ca(OH)_2$$

Basic anhydride alkali

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

acidic anhydride acid

$$CaH_2 + H_2O \longrightarrow Ca(OH)_2 + H_2$$

$$SiCl_4 + 2H_2O \longrightarrow SiO_2(s) + 4HCl(aq)$$

$$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + HC \equiv CH$$

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

$$Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2NH_3$$

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

Due to hydrolysis different salts behave acidic or alkaline e.g.

$$Na_2CO_3(s) + H_2O \longrightarrow \underset{\text{(alkaline)}}{2NaOH} + H_2CO_3$$

$$NH_4Cl + H_2O \longrightarrow NH_4OH + \underset{\text{(acidic)}}{HCl}$$

→ Water as hydrates : $CuSO_4.5H_2O$

$[Cu(H_2O)_4]SO_4.\ H_2O$, water as a ligand & hydrate.

Tetraquo copper (II) sulfate. monohydrate.

HOME ASSIGNMENT

1. Explain :
   - (i) Water acts as an amphoter.
   - (ii) hydride salt liberates hydrogen on electrolysis and hydrolysis.
   - (iii) Ice floates over water.
   - (iv) Ammonia is a covalent compound but soluble in water.
   - (v) Water is a liquid but H_2S a gas.
2. What are hybrides ? study these compounds.

L-82

* **Hard and Soft water -**

Soft water - That produces good lather with soap readily. eg. rain water, distilled water.

Hard water - does not produce good lather with soap. eg. Lake water, well water, pond water.

→ Cause of hardness of water - (presence of Ca^{++} and Mg^{2+} in water)

In presence of soap it forms insoluble salt.

$$2\,C_{17}\,H_{35}\,COO^{-}\,Na^{+} + Ca^{2+} \longrightarrow \left(C_{17}^{1}\,H_{35}COO\right)_2 Ca \downarrow + 2Na^{+}$$

Soap (Sodium stearate) similar with Mg^{2+}.

→ Types of hardness :

(a) Temporary - Presence of bicarbonates of Ca^{++} & Mg^{2+}

[carbonate hardness]

removal - simply by boiling.

(b) Permanent hardness - Presence of soluble Cl^{-} & sulphates of Ca^{++} and Mg^{2+}

Softening or removal of hardness.

(i) lime soda process - (Ca^{++} and Mg^{2+} ions are removed as carbonates)

(ii) Ion - exchange process - permutit process using zeolite (sodium aluminium silicate - $Na_2Al_2Si_2O_8.XH_2O$

* **Heavy water :** Protium water gets ionised 13.4 times faster than heavy water (D_2O). By repeated electrolysis of ordinary water taking nickel electrodes the unionised D_2O can be separated.

Properties : $Na + D_2O \longrightarrow 2NaOD + D_2$

[identical to that of hydrogen] Sodium deutro oxide

- Reaction with CaC_2

$$CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + C_2D_2 \quad \text{Heavy acetylene}$$

- Exchage reaction -

$$HCl + D_2O \rightleftharpoons DCl + HOD$$

$$NaOH + D_2O \rightleftharpoons NaOD + HOD$$

- Reaction with acid an hydride -

$$SO_3 + D_2O \rightarrow D_2SO_4 \text{, Deutrosulfuric acid.}$$

Uses : - As moderator to slow down the movement of neutron in atomic reactor.

- In product of deuterium.

* **Hydrogen peroxide.**

- Preparation of H_2O_2 from peroxide.

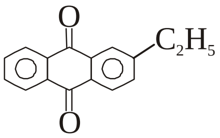
$$BaO_2 + H_2SO_4 \xrightarrow{\text{ice cold}} BaSO_4 \downarrow + H_2O_2$$

$$BaO_2 + CO_2 + H_2O \longrightarrow H_2O_2 + BaCO_3 \downarrow$$

- Electrolysis of 50% H_2SO_4 - At anode : $HSO_4^{-} - e^{-} \rightarrow HSO_4$

$$HSO_4 + HSO_4 \rightarrow H_2S_2O_8$$

$$H_2S_2O_8 + 2H_2O \rightarrow H_2O_2 + 2H_2SO_4$$

- From 2-ethyl anthraquinol $\xrightarrow[Pt]{O_2}$ hydrogen peroxide + 

* Concentration of H_2O_2 : The hydrogen peroxide formed contains H_2O as impurity which can be separated by fractional evaporation at 373 K. Then placed in side dessicator containing anhydrous $CaCl_2$ or conc. H_2SO_4.

* Properties :

(a) acidic nature : $\underset{\text{acid}}{H_2O_2} + \underset{\text{alkali}}{2NaOH} \longrightarrow Na_2O_2 + 2H_2O$

$$H_2O_2 + Na_2CO_3 \longrightarrow Na_2O_2 + H_2O + CO_2$$

(b) Oxidising nature :

$$H_2O_2 \longrightarrow H_2O + O$$

acidic medium $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$

alkaline medium $H_2O_2 + 2e^- \longrightarrow 2OH^-$

(i) With PbS

$$H_2O_2 \longrightarrow H_2O + O$$
$$\underline{PbS + 4(0) \longrightarrow PbSO_4}$$

(ii) with KI -

$$2e^- + H_2O_2 \longrightarrow 2OH^-$$
$$\underline{2I \longrightarrow I_2 + 2e^-}$$

(iii) with Na_3AsO_3 -

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$$
$$\underline{AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e^-}$$

(iv) with potassium ferrocyanide -

$$\left[Fe(CN)_6\right]^{4-} \longrightarrow \left[Fe(CN)_6\right]^{3-} + e^-$$

(c) Reducing nature :

(i) $Ag_2O + H_2O_2 \longrightarrow H_2O + 2Ag + \frac{1}{2}O_2$

(ii)

$$Cl_2 + 2e^- \longrightarrow 2Cl^-$$
$$\underline{H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-}$$

(d) decolorised acidified $kMnO_4$ solution

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$
$$\underline{MnO_4^- + 8H^+ + 5e^- \longrightarrow M_n^{2+} + 4H_2O}$$

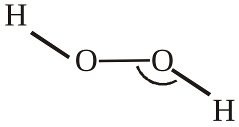
(e) It reduced $K_2Cr_2O_7$ (solution) to form green colored solution of $Cr_2(SO_4)_3$.

$$Cr_2O_7^{=} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

(f) Ferricyamide getting reduced to ferrocyamide.

$$\left[Fe\left(Cv\right)_6\right]^{3-} + e^- \longrightarrow \left[Fe\left(CN\right)_6\right]^{4-}$$

* Structure



Half-open book structure.

* **Strength of H_2O_2**

20 volume : i.e., 1 ml of '20 vol of H_2O_2' provides 20 ml of oxygen at NTP. X-vol. of H_2O_2 : i.e. 1 ml of it gives X ml of O_2 at NTP

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

68 gram 22400 ml at NTP

22400 ml at NTP given by 68 gram H_2O_2

$$\text{X ml at NTP given by } \frac{68}{22400}.\text{X gram}.$$

$$\text{1 ml of 'X vol' gives X ml of } O_2 \text{ i.e. } \frac{68\,X}{22400}\text{gram}.$$

$$\text{1000 ml 'X vol' gives } \frac{68\,X}{22400} \times 1000 = \frac{68\,X}{224}$$

$$\boxed{\text{gram}/L = \text{Strength} = \frac{68\,x}{224}}$$. X = volume strength of H_2O_2(aq).

$$\text{20 vol. of } H_2O_2 = \frac{68 \times 20}{224} = 6.07\,\text{gram}/L$$

* Uses of H_2O_2 – Any two uses

* **Hydrogen as fuel :** Due to high enthalpy of combustion, it's considered as an ideal rocket fuel.

→ Advantages : Any two.

→ Hydrogen economy : Recent research works are under progress to identify economically viable and safe sources of dihydrogen for its use as a commin source of energy.

HOME ASSIGNMENT

1. **(a)** Provide a test to identify H_2O_2 as

(i) an acid (ii) an oxidant and (iii) a reductant.

(b) Calculate the normality and molarity of '20 volume of H_2O_2'.

(c) Write two uses of heavy water.

(d) Why hard water fails to form good lather with soap ?

(e) Complete the following :

$$Na + D_2O \longrightarrow$$

$$CO_{(g)} + H_2(g) \xrightarrow[\text{Catalyst}]{\text{Cobolt}}$$

UNIT - X

(s-BLOCK ELEMENTS)

L-83, L-84

s - block → ns^1 group -1 Alkalimetals
ns^2 group - 2 Alkaline earth metals
n = 2 to 7

* **Elements & their electronic configuration :**

Alkalimetals, Li, Na, K, Rb, Cs, Fr^* ($n\ s^1$ whose n = 2 to 7 indicating the period number). **Group-2,** Be, Mg, Ca, Ba, Sr, Ra (ns^2)

* **Occurrence** Both the metals present in Group 1 and group -2 are reactive and don't occur in free state but widely distributed in nature is combined state; silicates, carbonate, sulfate etc. Alkali metals and alkaline earth metaly [except KCl. $MgCl_2.6H_2O$] and dolomite ($Mg\ CO_3\ CaCO_3$) do not occur together.

Metals abundantly present (in the form of compounds): Ca (5th), Mg (6th), Na(7th), K (8th), Ba(14th) and Sr (15th) most abundant. Sea water contains 2.8% NaCl and 0.8% KCl.

* Anomolous behavious of first element of group 1 and 2 Reasons for the difference :

(i) Small atomic or ionic radii

(ii) high electrogenative and ΔiH value.

(iii) high polarising power of cation i.e. charge / unit area = $\dfrac{\text{ionic charge}}{\frac{4}{3}\pi\,(\text{ionic radius})^2}$

thus polarising power $\propto \dfrac{\text{ionic change}}{(\text{its radius})^2}$

(iv) absence of d-electrons in its valence shell

e.g. Li & Be differs from other elements of group 1 and Group 2 respectively.

(v) Acting as powerful reducing agent even if high ΔiH value. This is due to greater $\Delta_{hyd}H$ value as ions can easily hydrated out of ion-dipole $\left(:\ddot{O}\begin{matrix}/H\\ \backslash H\end{matrix}\right)$ attraction.

$E^0_{Li^+_{(aq)}|Li}$ and $E^0_{Be^{2+}_{(aq)}|Be}$ values are highly negative.

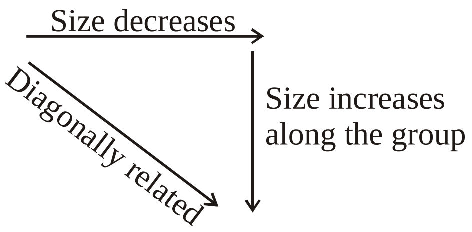
* **Diagonal relationship :**

$$\begin{tikzcd} Li \arrow[dr] & Be \arrow[dr] & B \\ Na & Mg & Al \end{tikzcd}$$

This similarities are weaker than the similarities found within the group.

Reasons : (i) Similarity in electropositive character (electronegativity values)

(ii) Similarity in atomic atomic/ions radii



(iii) Comparable polarising power.

Example : (i) Li and Mg form nitrides

(ii) Li_2O and MgO never form superoxide.

(iii) Li_2 CO_3 and $MgCO_3$ decompose librating CO_2.

(iv) Li & Mg do not form solid bicarbonate

(v) Li Cl and $MgCl_2$ soluble in alcohol due to covalent nature.

(vi) Li Cl amd MgC_2 are deliquescent. The hydrates are $LiCl.2H_2O$ and $MgCl_2.8H_2O$

Such propertes differ along the group $\left(\text{Li} \rightarrow \text{Na and Be} - \text{Mg}\right)$

L-84

Trens in variation of properties along the group (1 & 2)

(i) Atomic and ionic radii : gradually, **increase** on moving down the group with increasing of shell number. The ions are having noble gas configuration. Alkali metal cations are largest in their respective period, the size smaller than the corresponding atom.

$$\begin{array}{ccc} r_{Li^+} & & r_{Li} \\ Is^2(He) & < & Is^2 2s^1 \end{array}$$

(ii) ΔiH values of alkali metals are low due to bigger atomic size, however the values gradually **decreases** down the group from Li to Cs. Due to noble gas configuration of M^+ $\left(\Delta iH\right)_2$ is very very high.

(iii) M.P. and B.P. : All these metals are soft and have low melting and boiling point as the ions / atoms are loosely packed in the crystal lattice due to bigger size and presence of single valence electron (lower metallic bond strength). The density gradually increases of Li to Cs.

(iv) Flame coloration : All these metal (Chloride salt) imparts different colour to the flame due to low ΔiH value and the electronic transitions occurs in the visible spectral zone. The complementary colour of the absorbed one is visualised e.g. Na (yellow) and K (pale violet as $r_K > r_{Na}$.

(v) Lattice energy of MCl.

$$\Delta_{lat.}H \quad LiCl > NaCl > KCl > RbCl > CsCl$$

$$r_+ \quad Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$$

(vi) $\Delta_{hyd}.H$ (depends on greater charge and smaller size)

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$

* **Chemical property :**

The high chemical reactivity is due to

(i) Lower ΔiH

(ii) Low heat of atomisation, $\Delta_{atom}.H$

(iii) Much lower reduction potential value

e.g $E^0_{Li} | Li^+_{(aq)} = +3.04\,V$ (Higher oxidation potential)

→ Action with air to form oxides :

$4\,Li + O_2 \rightarrow 2\,Li_2O$ (Monoxide)

$2Na + O_2 \rightarrow Na_2O_2$ (Peroxide)

$M + O_2 \rightarrow MO_2$ (super oxide)

M = K, Rb and Cs

Small cation can stabilise smaller anion and a large cation can stabilise bigger anion. Lithium forms oxide but fails to form peroxide. Li^+ is smaller has strong positive field around it & can combine with smaller O^{2-} (oxide) ion but fail to combine with bigger peroxide ion $[–O–O–]^{2–}$, weak negative field.

Due to high reactivity these metals normally kept inside kerosine oil. Lithium is kept inside wax, as it's lighter, it floates over kerosine and exposed to air to tarnish.

→ $2M + H_2 \longrightarrow 2MH$

Stability of the hydride LiH > NaH > KH > RbH > CsH due increase of M – H bond length.

These are all better reducing agents, CsH> RbH > KH > NaH > LiH

→ With water - form hydroxide liberating $H_{2(g)}$. These hydroxids are strong alkalis & Basic character increases from Li to Cs.

→ With halogen : $2M + X_2 \longrightarrow 2MX$

Reactivity increases from Li to Cs due to decrease of ΔiH value.

Ionic character of Li halides : LiF > LiCl > LiBr > LiI

I is more polarisable due to bigger size & hence more covalent in character. All halides except LiF are soluble in water. LiF has high lattice energy due to small cation and small anion.

→ With liquid NH_3.

$$M + (x+y)NH_3 \longrightarrow \left[M\left(MH_3\right)_x\right]^+ + \left[e^-\left(NH_3\right)_y\right]$$

On standing, the solution slowly liberates hydrogen gas.

$$2M + 2MH_3 \longrightarrow 2MNH_2 + H_2$$

metal amine

The solution conducts electricity (formation of ions) & look blue due to ammoniated electron.

→ Reducing nature – Alkali metals are strong reducing agents.

$2Li + 2C_2H_5OH \rightarrow 2\ LiOC_2H_5 + H_2 \uparrow$

Alcoholic sodium (C_2H_5OH + Na) acts as common reducing agent in organic chemistry.

$2Na + HC \equiv CH \longrightarrow NaC \equiv CNa + H_2$

* **Uses :**

→ White metal, Li -Pb alloy others are LiAl, LiMg.

Li also used in thermo nuclear reactions and to make electrochemical cells.

→ Na-Pb alloy to make organo - Lead compounds earlier used as anti knock reagent.

→ Na(*l*) used as coolant is fast breeder reactor.

→ Potassium plays vital role in biological system. KCl used as a ertiliser. KOH is used to prepare soft soap. It also absorbs CO_2.

→ Cs is used in devising photoelectric cells.

HOME ASSIGNMENT

(a) Diuscuss the magnetic behaviour of O_2^{2-} and O_2^{-}.

(b) Explain the following :

(i) NaCl is highly soluble in water while LiCl is less soluble.

(ii) Cs is used in photo-electric cell.

(iii) Sodium metal is kept inside kerosine.

(iv) Sodium metal being dissolved in $NH_3(l)_a$ looks blue and conducts electricity.

(v) Lithium has higher ΔiH value but it is powerful reducing agent.

(vi) Lithium differs from other elements of the group.

(vii) Na imparts yellow where potassium imparts violet flame coloration.

(viii) Lithium fails to form peroxide.

(ix) Lithium is diagonally related to Mg.

(x) Electrical conductivity of aqueous chlorides of alkali metal increases from Li to Cs.

*** L-85**

Preparation of $Na_2CO_3.10H_2O$ (washing soda) Ammonia soda prcess: (Solvay process)

$$NH_{3(aq)} \xrightarrow{CO_2} (NH_4)_2\,CO_{3(aq)} \xrightarrow{CO_2\,(excess)} NH_4HCO_3\,.$$

$$\xrightarrow{NaCl} NaHCO_3 \xrightarrow[\Delta]{} Na_2CO_3$$

* $KHCO_3$ can't be prepared by solvay process as $KHCO_3$ is too soluble to be precipitated by NH_4HCO_3 to form a saturated solution with KCl.

sodium Carbonate

$$\xrightarrow{H_2O} NaOH + H_2CO_3 \text{ (strongly alkaline)}$$

$$\xrightarrow{HCl} NaCl + H_2O + CO_2$$

$$\xrightarrow{CO_2 + H_2O} NaHCO_3$$

$$\xrightarrow{SiO_2} Na_2SiO_3 + CO_2$$

$$\xrightarrow{BaCl_2} BaCO_3 + NaCl$$

$$\xrightarrow{CuSO_4} CuCO_3 + Na_2SO_4$$

$\xrightarrow{\Delta}$ No change (Alkali metal carbonates except Li_2CO_3 are thermally stable while bicarbonates are thermally unstable.

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$$

* **Sodium chloride :** (Solar) Evaporation of Sea water 2.7 to 2.0 massy. NaCl

Impurities : $MgCl_2$, $MCaCl_2$, Na_2SO_4, $CaSO_4$

$MgCl_2$ and $CaCl_2$ are deliquescent (absorb moisture)

Hence it turns into liquid (solution) specially is rainy season.

Purification : Crude salt is dissolved in minimum quantity of water & filtered. The solution is then saturated with $HCl_{(g)}$. Due to common ion affect NaCl precipitats. Only KCl is present as impurity which is removed by repeated crystallisation.

* **Sodium hydroxide** (Caustic soda)

Principle - Electrolysis of sodium chloride solution (brine) with mercury cathods and carbon anode.

Thus in Castner - Kellner Cell at cathode :

$$Na^+ + e^- \xrightarrow{Hg} Na - \text{amalgam}$$

At anode $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$

$$Na - Hg + 2H_2O \longrightarrow 2NaOH + 2H_3 + H_2$$

It is deliquescent and on exposure converts to Na_2CO_3.

$$2NaO + CO_2 \rightarrow Na_2CO_3$$

Uses -
(i) Manufacture of different salts.
(ii) Lab chemicals.
(iii) In the purification of bauxite.

* **Sodium bi-carbonate** (Baking soda)

→ Preparation: Saturated solution of $Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$ Being less soluble, gets separated.

→ **Use -**

(i) In bakery as its decomposed to form CO_2 making the cakes or pastries light an fluffy.

(ii) Used in fire extinguisher.

* Biological importance of sodium and potassium.

70 kg man contains 90g of Na, 170 g of K cmpared to 5 gram of iron and 0.06 g. of Cu.

$Na^+ \rightarrow$ extracellular cation.

$K^+ \rightarrow$ intracellular cation (i.e., in the cell fluid)

→ **Function :** (i) Maintaining osmotic pressure : maintain the normal osmotic pressure of different body fluids & thus protects the body against excessive loss of fluids.

(ii) Maintaining proper viscocity of blood. NaCl & KCl present in the blood plasma help in keeping the globulins in physical solution and in regulating the degree of hydration of plasma proteins i.e., vital in maintaining proper viscosity of blood.

(iii) Secretion of digestive fluids - Gastric HCl derived from NaCl present in blood Na and K salts.

(iv) Na^+ and K^+ differ quantitatively in their ability to activate enzymes in their transport mechanism and in penetrating the cell membrane.

HOME ASSIGNMENT

(a) How can you prepare (i) caustic soda from NaCl

(ii) backing soda from washing soda.

(b) Fill in the gaps .

(i) Between Na, K, Fe, Cu _______ present in the body to a greater extent.

(ii) _________ is used in manufacture of soap.

(iii) _________ gas is evolved on decomposition of $NaNO_3$.

(iv) $LiNO_3$ on decomposition forms _________ and _______ gases.

(v) _________ is a power ful reducing agent among the alkali metals.

(c) Identify the gases evolved in the Castner - Kellner Cell.

(d) Write down the molecular formula of washing soda, baking soda, glauber salt, caustic potash, caustic soda, brine, microcosmic salt, Rochelle salt.

(e) Choose the incrreoct statement :

(i) Thermal decomposition of $NaNO_3$ gives $NO_{2(g)}$ and $O_{2(g)}$

(ii) Lithium fails to form ethynide with ethyne.

(iii) LiF and Li_2O are less soluble in water.

(iv) LiCl and $MgCl_{-2}$ are deliquescent.

(v) $LiHCO_3$ is not obtained in solid state.

L-86-87

Alkaline earth metals (Be, Mg, Ca, Sr, Ba and Ra :

→ Electronic configuration. ns^2 n = 2 to 7

→ Atomic and ionic radii. increases from Be to Ra

→ Ionisation enthalpy : decreases due to increasing of atomic size.

$$\Delta_i H_1 > \Delta_i H_1 \text{ (alkali metals)}$$

→ $\Delta_{hyd.}H.$ $Be^{2+} > Mg^{2+} > Ca^{2+} > S_r^{2+} > Ba^{++}$

This depends on (i) smaller size and higher charge $\left[\Delta_{hydr.}H\right]_{\text{alkaline earth metals}} > \left[\Delta_{hydr.}H\right]_{\text{alkali metals}}$

e.g. $MgCl_2$. $6H_2O$ and $CaCl_2.6H_2O$, NaCl and KCl don't have hydrates.

→ Flame coloration - Be & Mg due to smaller size and higher $\Delta_i H$ value fails to impart flame colouration Ca (Bickred), Sr (crimson) Ba(pea green)

→ Bivalent ions : (inspite of the fact that $\Delta_i H_2 > \Delta_i H_1$)

Reason : (i) M^{2+} (stable noble gas configuration) e.g. Mg^{2+}(Ne)

(ii) $\Delta_{hydr.} M^{2+} > \Delta_{hydr.} M^{+}$

(iii) Lattice energy : divalent ion forms stronger lattice than monovalent. Energy releases in above (ii) & (iii) compensates high second ionisation enthalpy.

* **Chemical properties :** These are less reactive than alkali metals. However the chemistry is mainly dominated by M^{2+} ions.

→ **Action with air (or) oxygen** (Formation of oxides)

Mg burns in **air** with dazzling brilliance to fom MgO and Mg_3N_2. React with **water** to form hydroxide.

$$M_g + O_2 \longrightarrow 2M_gO, \qquad M_gO + H_2O \longrightarrow M_g(OH)_2$$

$$3M_gN_2(\text{air}) \longrightarrow Mg_3N_2,$$

$$Mg_3N_2 + 6H_2O \longrightarrow 3M_g(OH)_2 + 2NH_3 \uparrow$$

$$Mg + 2H_2O \longrightarrow M_g(OH)_2 + H_2 \uparrow$$

The reactivity decreases from Be to Ba.

The alkalinity increases from Be to Ba. $Ba(OH)_2 > Sr(OH)_2 > Ca(OH)_2 > M_g(OH)_2$

BeO and M_gO are almost insoluble in water due to large lattice energy.

BeO is amphoteric : $BeO + 2HCl \rightarrow BeCl_2 + H_2O$

Base

$BeO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$

acid

→ Action with halogen :

$$M + X_2 \rightarrow MX_2 \left(X = F,\ Cl, Br,\ I\right)$$

* BeF_2 is prepared on thermal decomposition of $(NH_4)_2BeF_4$ $BeCl_2$ is prepared from BeO : $BeO + C + Cl_2 \xrightarrow{\Delta} BeCl_2 + CO$. $BeCl_2$ (vapour phase) present as chloro bridged dimer.

In solid state it exists as chain polymer.

These chloride present as hydrates but halide hydrates decreases on moving down the group.

$$MgCl_2.8H_2O \ \ CaCl_2.\ 6H_2O,\ BaCl_2.\ 2H_2O$$

* $BeCl_2$ & $MgCl_2$ hydrates on heating hydrolyse.

$$M_gCl_2.8H_2O \longrightarrow Mg(OH)_2 + HCl$$

$$BaCl_2.2H_2O \longrightarrow BaCl_2\ \text{(anhydrous)} + 2H_2O$$

* The fluorides are relatively less soluble than the chlorides owing to their high lattice energies.

→ Action with hydrogen

Except Be other react with H_2 to form ionic hydride.

BeH_2 is prepared from $BeCl_2$.

$$2BeCl_2 + LiAlH_4 \longrightarrow 2\,BeH_2 + LiCl + AlCl_3$$

$$Ca + H_2 \xrightarrow{\Delta} \underset{\text{(hydrolith)}}{CaH_2} \xrightarrow{H_2O} Ca(OH)_2 + H_2$$

→ **Reducing nature :** Reducing power of alkaline earth metals is less than that of alkali metals. $E^0_{M^{2+}_{(aq)}}\,|\,M$ is largely negative.

$E^0_{Be^{2+}}\,|\,Be = -1.97V$ $\qquad E^0_{Mg^{2+}|Mg} = -2.36V$

Lower negative potential value is due to (i) higher hydration enthalpy for smaller ionic size.

(ii) Large value of atomisation.

→ Reduction potential of any element based on following factors :

$$\begin{tikzcd} M_{(s)} \arrow[r, "\Delta_{atoms.}H", "+ve"'] & M_{(g)} \arrow[r, "\Delta_i H", "+ve"'] & M^{n+}_{(g)} \arrow[d, "\Delta_{hyd.}H"', "(H_2O)\ (-ve)"] \\ M_{(s)} \arrow[rr, shift right, "Oxidation"'] & & M^{n+}_{(Aq)} \arrow[ll, shift right, "E^0_{M^{n+}_{(aq)}|M}"', "Reduction"] \end{tikzcd}$$

* **Salts of oxoacids :**

Carbonates : * solubility decreases on moving down the group.

$BeCO_3$ is soluble but $BaCO_3$ is insoluble as lattice energy remains almost same but the hydration energy decreases with increased ionic size.

* Thermal stability :

$$\underset{\sim 373K}{BeCO_3} < MgCO_3 < CaCO_3 < SrCO_3 < \underset{(1633K)}{BaCO_3}$$

$$MCO_{3(g)} \xrightarrow{\Delta} MO_{(s)} + CO_{2(g)}$$

- On passing excess $CO_2(g)$ soluble bicarbonates are formed.

$$\underset{\text{insoluble}}{MCO_3} + CO_2 + H_2O \longrightarrow \underset{\text{soluble}}{M(HCO_3)_2}$$

- Lime stone decomposes to form quick lime.

$$CaCO_3(s) \longrightarrow CaO_{(s)} \longrightarrow CaO_{(s)} + CO_2,\ \Delta H = +42\,\text{cal/mol}.$$

Used as flux in **smelting ores.** (Iron extraction)

CaO removes SiO_2 (impurity) as $CaSiO_3$ (slag).

Sulfates : * Thermally stable

* $BeSO_4$ and $MgSO_4$ are water soluble but the solubility decreases from $CaSO_4$ to $BaSO_4$. High hydration enthalpy of smaller Be^{2+} and Mg^{2+}.

Nitrates : $MCO_3 + 2HNO_3 \longrightarrow M(NO_3) + CO_2 + H_2O$

$$M(NO_3)_2 \longrightarrow 2MO + 4NO_2 + O_2$$

* **Anomalous behaviour of Be.**

(i) Small size, high electro negativity, high ΔiH value high polarising power hence mostly from covalent compounds.

(ii) Be has maximum covalency state four but other can have six due to presence of d-orbitals.

Be (4) $1s^2\ 2s^1\ 2p_x^1\ 2p_y^0\ 2p_z^0$ (Four valence state)

e.g. $BeF_2 + 2F^- \longrightarrow [BeF_4]^{2-}$ tetrafluorido beryllate (II)

(iii) BeO and $Be(OH)_2$ are **amphoteric** while others are increasingly basic.

(iv) Be_2C on action with water gives methane while MgC_2 give C_2H_2 (acetylene)

(v) Be due to its low reactivity fails to react with water and acid while other form $H_2(g)$.

* **Diagonal relationship with Al :**

Some of the similarities:

(i) $Be(OH)_2$ dissolves in excess of alklai to give beryllate ion, $[Be(OH)_4]^{2-}$ just as Al gives $\left[Al(OH_4)\right]^-$, aluminate ion.

(ii) Be and Al have Cl^- bridged structure in vapour phase. Both the chlorides are soluble in organic solvents and are strong Lewis acids. They are used as Friedel Crafts catalyst.

(iii) Be and Al ions can fom complexes $[BeF_4]^{2-}$, $[AlF_6]^{3-}$ because of identical polarising power.

(iv) BeO and Al_2O_3 are amphoteric in nature.

These are high melting insoluble solids.

(v) Be_2C and Al_4O_3 on hydrolysis form methane (g).

* **Biological importance of Mg and Ca :**

An adult body contains about 25 g of Mg and 1200 g of Ca compounds.

Functions :

(i) Chlorophylll, the green pigment of plant, contains magnesium, which makes photosynthesis possible.

(ii) All enzyme that utilise ATP in phosphate transfer require Mg as Co-factor.

(iii) About 99% of body calcium present in bones and teeth.

(iv) Calcium plays an important role in clotting of blood and stabilisation of protein structure.

(v) Calcium finds its use in the functing of neuro - muscular and interneuronal systems.

HOME ASSIGNMENT

1. (a) Fill in the blank :

(i) Element ____ group differs from the other element of group-2, but it relates mostly with ______ group diagonally.

(ii) The maximum valence state of Mg is _________.

(iii) The metal present in Chlorophyll is _________.

(iv) _______ foms unstable carbonate while ____ is the most stable carbonate of group-2.

(v) The water of crystallisation of $BaCl_2$ is _________.

(b) Match the following coloumns :

	[A]	**[B]**
(i)	Bone	1. BeF_2
(ii)	Amphoteric oxide	2. $Mg(OH)_2$ suspension
(iii)	Bleaching powder	3. Calgon
(iv)	Milk of magnesia	4. Calcium
(v)	Thermal decomposition of ammonium tetra fluoridoberyllate	5. Aluminium oxide
		6. Calcium hypochlorite

(c) Write the molecular formulae of -

(i) gypsum (ii) plaster of paris (iii) Quick lime (iv) slaked lime

(d) Arrange the following in order of increasing character as mentioned below :

(i) Carbonates of group 2. in order of increasing solubility in water.

(ii) Hydroxides of group-2 in order of increasing basic nature.

(iii) Thermal stability of carbonates of alkaline earth metals.

(iv) $\Delta_{hydr.}H$ value of cations of group-2.

(v) Reactivity of alkaline earth metals with oxygen.

(e) Give reasons :

(i) $BeCl_2$ is covalent exists as a chain structure.

(ii) $BeSO_4$ is soluble but $BaSO_4$ is insoluble.

(iii) Anhydrous $MgCl_2$ cann't be prepared on heating $MgCl_2.8H_2O$.

UNIT - XI

SOME p-BLOCK ELEMENTS

L-88, L-89 [group-13 elements]

p-block elements (Representative / normal elements)

Where electrons are subsequently enter into outermost (nth) shell of the atom. (np^1 to np^6) n = 2 to 7 indicating the period number.

→ General characteristics of p-block : oxidation state, metallic character covalency.

* **Borow family :**

→ Electric configuration : B_5 $Al_{(13)}$ $Ga_{(31)}$ $Tn_{(49)}$ $Tl_{(81)}$

→ Occurrence : *$^{10}_{5}B$ (19%) and $^{11}_{5}B$ (81%). Its abundance in earth's crustis only 0.0001 % by mass. It occurs as Borax ($Na_2\ B_4O_7.10\ H_2O$) Kernite ($Na_2B_4O_7.\ 4H_2O)_g$ Colenanite ($Ca_2\ B_6\ O_{11}.\ 5H_2O$)

* Aluminium is the 3rd most abundant element (8.3%) after oxygen (45.5%) and silicon (27.7%) Ores of Al : Bauxite ($Al_2O_3.2H_2O$), Diaspore ($Al_2O_3.H_2O$)

Corundum (Al_2O_3), Sapphire (Al_2O_3)
Cryolite (Na_3AlF_6)
Felspar $KAl\ Si_3O_8$
Spinel MgO, Al_2O_3

* **General characteristics :**

→ Atomic radii - * Al(143 pm), Ga (135), ln (167) Abnormal decrease of atomic radius of Ga instead of increase in due to introduction of 3d^{10} which have less screening effect. So size decreaases due to increases of Z^*

(ENC) . $Z^* = (Z - \sigma)$, σ = screening constant

$\sigma_{s > p > d > f}$.

Less is the 'σ' more is the Z^*, atomic size decreases due to increase of nucleus - 'e' attraction.

* In (167 pm) Te (170 pm), aa small increase may be accounted for introduction of 4f electrons which have further more screening effect.

→

ΔiH values :		B	Al	Ga	ln	T*l*
kJ/mol	ΔiH_1	801	577	579	558	589
	ΔiH_2	2427	1816	1979	1820	1971
	ΔiH_3	3659	2744	2962	2764	2877

i.e., $\boxed{B > Al < Ga > ln < T\ell}$

Observation :

(i) There is generally decrease of $\Delta_i H$ value with increase atomic size (n value)

(ii) The trend is not regular due to low screening of 'd' and 'f' electrons, that increases the ENC (z)

$Al = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

$Ga = 2,\ 8,\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^1$

Similarly the increase of $\Delta_i H$ value of Tl is due to introduction 4f electrons which have further low screening effect. Due to imperfect shielding of the nucleus by the extranuclear electrons the effective nuclear change $(Z - \sigma)$, σ = screening constant (low value) increases increasing force of attraction between the nucleus & the out going valance electron and increases the ΔiH value.

(iii) Abnormal high value of ΔiH_2 is due to removal of second electron from such penetrated ns orbital, so also in case of ΔiH_3. First electron is to be removed from p-orbital. (ns^2np^1). Thus $\Delta_i H_3 > \Delta_i H_2 >> \Delta_i H_1$

→ **Electronegativity :** Down the group electrovity first decreases from $B_{(2.0)} - Al_{(1.5)}$, then marginally and it increases $Ga_{(1.6)}$ $ln_{(1.7)}$ $Tl_{(1.8)}$. This is because of the discrepancies in atomic size of the elements. This indicates B is a matalloid.

→ Oxidation state : +3 (ns^2 sp^1). Boron can have –3 o.s in certain compounds because of their higher electronegativity value (boride). The heavier elements (down the group) exhibits variable o.s. of +1 and +3. $\left(Tl^+ > ln^+ > Ga^+\right)$. This is due to iner pair effect i.e. s^2 electron normally fails to take part in bond formation.

*. Chemical properies : All elements form M^{3+} compounds. The tendency to form M^+ compounds gradually increases down the group. As per Fajan's rule +3 statae (B^{3+}) compounds are more covalent due to greater polarising power (smaller size & greater change). However, Al^{3+}, Ca^{3+} and Tl^{3+} give ionic compounds. Tl^+ ion is quite stable.

→ Action with air : Boron is unreactive in crystalline form. Al form a thin layer of oxide. Amorphous boron and Al metal on heating with oxygen form B_2O_3 and Al_2O_3.

$$2E + 3O_{2(g)} \xrightarrow{\Delta} 2E_2O_3(s)$$

$$2E + N_{2(g)} \xrightarrow{\Delta} 2EN \qquad \left(E = \text{element}\right)$$

B_2O_3 (acidic), Al_2O_3 & Ga_2O_3 (amphoteric), ln_2O_3 and Tl_2O (Basic)

→ **Action with H_2 :** No direct reaction with H_2, but indirectly hydride can be formed. the stable hydids of boron are called borane (i) B_nH_{n+4} type : B_2H_6, B_5H_9 etc.

(ii) B_nH_{n+6} type : B_4H_{10}, B_5H_{11} etc.

$$ABF_3 + 3\ LiAlH_4 \rightarrow \underset{\text{(diborane)}}{2B_2H_6} + 2\ LiF + 3\ HlF_3$$

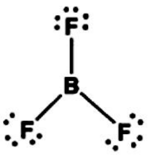
Tl does not form hydride. B, Al and Ga form complex hydride, $[AlH_4]^-$ e.g. $Na[BH_4]$, $Li[AlH_4]$ etc. These are electron deficient (Lewis acid and powerful reducing agent)

→ Action with halogen :

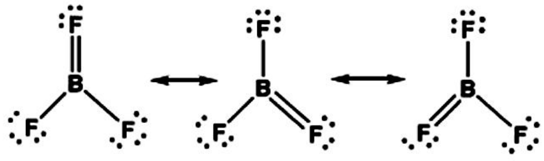
$$2E(\text{except Tl}) + X_2 \longrightarrow \underset{\text{(Lewis acids)}}{2EX_3}$$

$$\text{e.g. } \underset{\text{planner}}{H_3N: + BF_3} \longrightarrow \underset{\text{tetrahedral}}{H_3N: \rightarrow BF_3}$$

Acidic nature boron halides. $BF_3 < BBr_3 < BI_3$



A



B

Due to back donation, the e^- density at 'B' increases through π bond, overlaping of filled p-orbital of F and vacant p-orbital of 'B'.

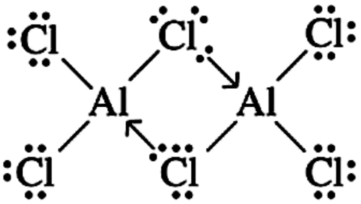
Hence inspite the –I effect the acidic nature becomes Less.

* hydrolysis of halide-

$$BCl_3 \xrightarrow{\text{hydrolysis}} \left[B(OH)_4^-\right]$$

$$AlCl_3 \text{ (or) } Al_2Cl_6 \xrightarrow{H_2O} \left[Al(H_2O)_6\right]^{3+} \text{ hexa aqua aluminate (III)}$$

Trihalides of Al, Ga and In exist as dimer e.g. Al_2Cl_6 in vapour state.



* Stability of monohalide : TlX > lnX > GaX (Ionic character increases on moving down the group).

→ **Action with acid and alkali :**

With HCl ; B and Tl (No reaction), Al dissolves liberating $H_{2(g)}$

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_{2(g)}$$

With H_2SO_4 : $2B + 3H_2SO_4(\text{conc.}) \xrightarrow[\Delta]{} 2H_3BO_3 + 3SO_2$

Boric acid

$$3H_2O + B \longrightarrow BO_3^{3-} + 6H^+ + 3e^-$$

$$4H^+ + SO_4^{2-} + 2e^- \longrightarrow SO_2 + 2H_2O$$

Al (No action with dil. H_2SO_4), show reaction with hot dil HCl.

Conc. H_2SO_4 liberated SO_2

$$2Al + 3H_2SO_4(\text{dil}) \xrightarrow{\Delta} Al_2(SO_4)_3 + 3H_2$$

$$2Al + 6H_2SO_4(\text{Conc}) \longrightarrow Al_2(SO_4)_3 + 3SO_2 + 6H_2O$$

With HNO_3 : Al becomes passive due to formation of a thin oxide layer. In reacts with all acids. Tl reacts with H_2SO_4 and HNO_3

With NaOH : B (No action)

$$2\,Al + 2\,NaOH + 6H_2O \longrightarrow 2\,Na^+\left[Al(OH)_4\right]^- + 3H_2O$$

Sod. tetra hydroxo aluminate (III)

* Anomalous property of BORON :

(i) Due to smaller size it forms covalent compounds.

(ii) Due to absence of d-orbitals it has maximum covalency four other can maximises upto six.

(iii) Due to sextet state it form Lewis acid, BCl_3 forms a large number of complexes due to its e^- accepting tendency.

(v) Exhibit –ve O.N. with active metals e.g. $3\,Mg + 2B \rightarrow Mg_3B_2$
(boride)

(vi) Form a number of stable hydrides called **borane.**

(vii) BCl_3 exists as a monomer while $AlCl_3$ as a dimer.

(viii) It is diagonally related to $Si(group - 14)$

* $B_2O_3 + 3H_2O \longrightarrow 2A_3BO_3$, $SiO_2 + H_2O \longrightarrow H_2SiO_3$

Boric acid metasilicic acid

* Boron form borane so alsosilicon form silane
(the hydrides of B and Si)

* Both oxides of B and Si can be reduced by Mg :

$$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$$

$$SiO_2 + 2Mg \longrightarrow Si + 2MgO$$

*** Boron and its properties :**

* Boron is a non metal with high m.p. (>2450K)

* Boron exhibits in different allotropic forms (4) e.g. B_{12}

* Boron with non metals:-

$$4B + 3O_2 \xrightarrow[\Delta]{} 2B_2O_3(s)$$

$$2B + N_{2(g)} \xrightarrow[\Delta]{} 2BN$$

$$2B + 3F_{2(g)} \xrightarrow[\Delta]{} 2BF_3$$

$$2B + 3X_{2(g)} \xrightarrow[\Delta]{} 2BX_3 \quad (X = Cl, Br, I)$$

* Action with metals (Ag, Au, Cd, Hg, Sn, Pb, Sb, Bi to form boride which are very hard with high melting point.

$$3M_{(s)} + 2B_{(s)} \xrightarrow{\Delta} Mg_3B_2(s)$$

$$Cr_{(s)} + B_{(s)} \longrightarrow Cr\,B(s)$$

* Reducing action - ${}_4B + 3CO_2 \longrightarrow 2B_2O_3 + 3C$

$$4B + 3SiO_2(s) \longrightarrow 2B_2O_3 + 3Si$$

→ Uses : * metal borides are used in atomic reactor for shielding ${}^{10}_{5}B$ absbs neutron in the reactor.

- * Boron fibers are used in air crafts.
- * lised to increase hardness of steel.
- * Boro compounds are becoming increasing important as rocket fuels due to high energy / weigh ratio.

* **Compounds of Boron.**

→ BORAX $Na_2 B_4O_7 . 10H_2O$ or $Na_2\left[B_4O_5(OH)_4\right].8H_2O$

* Preparation from colemanite ($Ca_2B_6O_{11}$)

$$\text{Powdered ore} \xrightarrow[\Delta]{Na_2CO_3(Aq)} \underbrace{Na_2B_4O_7 + \underset{\text{metaborate}}{NaBO_2} + CaO_3}$$

$$\downarrow \text{Filtered}$$

$$Na_2B_4O_7 + NaBO_2$$

$$\downarrow (CO_2)$$

$$Na_2B_4O_7 + Na_2CO_3$$

* $4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$

* Aqueous solution is alkaline.

$$Na_2B_4O_7 + 2H_2O \longrightarrow \underset{\text{Strong base}}{2NaOH} + \underset{\text{weak acid}}{H_2B_4O_7}$$

$$\underset{\text{Tetra boric acid}}{H_2B_4O_7} + 5H_2O \longrightarrow 4H_3BO_3$$

* Action of heat. (Boraxbead test)

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 \xrightarrow{\Delta} \underset{\text{metaborate}}{2NaBO_2} + \underset{\text{(Boricanhydride)}}{B_2O_3}$$

The glassy bead formed (in a pt. wire tip) impart different colour with different coloured salts. Knowing the bead colour salts of Ni^{2+}, Cu^{2+}, Cr^{3+}, CO^{2+}, Mn^{2+} can be identified in qualitative analysis.

$$B_2O_3 \xrightarrow{\text{Nickel salt}} \underset{\text{Nickel metaborate (brown)}}{Ni(BO_2)_2}$$

Uses :
- * As a mild antiseptic
- * Used in borax bead test to identify coloured salts.
- * Preparing optical glass
- * As a flux in soldering, welding.

→ **ORTHO BORIC ACID :** (H_3BO_3 - boric acid)

* Preparation (From borax)

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$$

Has layer structure in which planar BO_3 units are joined by H-bonds.

* Boric acid is a weak monobasic acid. It is not a protonic acid but a Lewis acid by accepting electron from a hydroxyl ion.

$$B(OH)_3 + 2HOH \longrightarrow [B(OH)_4]^- + H_3O^+$$

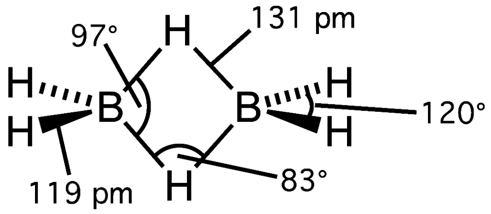
* Action of heat :

$$\underset{\text{Ortho}}{H_3BO_3} \xrightarrow[375K]{\Delta} \underset{\text{meta}}{HBO_2} \xrightarrow[433K]{\Delta} \underset{\text{Tetraboric acid}}{H_2B_4O_7} \xrightarrow{\text{red heat}} \underset{\text{Boric anhydride}}{B_2O_3}$$

Uses : Antiseptic, eyelotion in medicine

- Food preservative
- Candle industry to stiffen wicks and in tanning industry
- Making enamels in Pottery.

***** **Boronhydride** : Diborane ($B_2H_6 \rightarrow 12e^-$) is the simplest borane and analogous in molecular formula to C_2H_6 (ethane) $14e^-$. So diborane is electron deficient and form $2e^-$ three centre bond also called banana bonds.



$$2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$$

$$2BF_3 + 6NaH \xrightarrow[\Delta]{} B_2H_6 + 6NaF$$

→ Structure : There are two BHB bridge bonds while the four terminal H-atoms are in one plane along with two B.

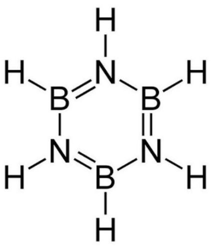
→ **Chemical properties :**

* $B_2H_6 + O_2 \longrightarrow B_2O_3 + 3H_2O + 1976\,kJ/mol$

* $B_2H_{6(g)} + H_2O(\ell) \longrightarrow 2B(OH)_3\,aq + 3H_2(g)$

* $B_2H_6 + N(CH_3)_3 \longrightarrow \underset{\text{adduct.}}{2BH_3.N(CH_3)_3}$

* $2B_2H_6 + 6NH_3 \longrightarrow \underset{\text{Borazine}}{2B_3N_3H_6} + 12H_2$ iso electronic - with benzene



- $B_2H_6 + NaH \xrightarrow[2]{(C_2H_5)O} 2Na^+[BH_4]^-$

  $B_2H_6 + 2LiH \xrightarrow{\text{ether}} 2\,\overset{+}{Li}[BH_4]^-$

- **ALUMINIUM :** Is a silvery-white, soft, nonmagnetic and ductile metal in boron group.
  - $2\,Al + 6HCl\,(dil) \longrightarrow 2Al^{3+}(aq) + 2Cl^-(aq) + 3H_2(g)$
  - $2\,Al + H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3 + 3H_2(g)$
  - Al becomes passive with conc. HNO_3 due to formation of an oxide layer.
  - $2\,Al + 2\,NaOH\,(aq) + 6H_2O \longrightarrow 2\,Na\,[Al(OH)_4] + 3H_2$

⟶ **USES :** Construction of air craft , railway coach, bus bodies, house hold utensils etc.

- Transmission cable in place of Cu.
- As wrappers for food materials, tobacco etc.
- Thermite welding: $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$.
- Alloy formation : Magnalium (Al + Mg)
- Duralumin Al + Cu + Mn + Mg

  Aluminium bronze - AH Cu

  γ – alloy Al + Cu + Mg + Mn

- ALUM : Alums are double salts with general formula

  $M_2SO_4 \,.\, T_2(SO_4)_3 \,.\, 24\,H_2O$

  M = monovalent ion like Na^+, K^+, Rb^+, Cs^+, NH_4^+, Tl^+

  T = Trivalent cation, Al^{3+}, Fe^{3+}, Cr^{3+}, Ga^{3+}, Co^{3+}.

e.g. potash alum : $K_2SO_4, Al_2(SO_4)_3 \,.\, 24H_2O$

Feric alum : $(NH_4)_2\,SO_4.Fe_2(SO_4)_3.2H_2O$

Chrome alum : $K_2SO_4.\; Cr_2(SO_4)_3.\; 24H_2O$

Uses : (i) as mordant in dyeing and calicoprinting.

(ii) Purification water (settling tank)

HOMEASSIGNMENT

1. Write the formulae of Borax, Potash alum, Boric acid, Corundum, tetraboric acid Boric anhydride.

2. What are alums ? Write one use of potash alum.
3. Thalium is stable in +1 oxidation state– explain.
4. What is thermite welding ?
5. Fill in the gaps :
   (i) $AlCl_3$ acts as Lewis ________.
   (ii) Boron carbide on hydrolysis liberated ________ gas.

(iii) $Al(OH)_3$ is _________ in nature.

(iv) The product formed by the reaction, $BCl_3 + H_2O \rightarrow$ is _______ .

(v) Aqueous solution of borax is _________.

6. Give reason :

(a) White fumes appear around the bottle of anhydrous $AlCl_3$.

(b) Boron unable to form BF_6^{3-}.

(c) Boric acid is considered as a weak acid.

(d) Tl^{3+} acts as powerful oxidant.

(e) ΔiH_2 of Al is exceptionally higher than ΔiH_1.

L-90 and L-91

CARBON FAMILY

* Introduction : Group 14 elements. Carbon family C, Si, Ge, Sn and Pb, Fl(114) constitute the carbon family. Fl (Flerovium) is a super heavy artificial chemical element with Z = H_4. It is an extremely radioactive synthetic element. IUPAC name - Ununquardium.

Carbon is the most abundant by mass of earth crust. It is the most versatile element in the world. It leads to another branch of chemistry, organic chemistry consisting of carbon compounds. Carbon has three isotopes ^{12}C, ^{13}C and ^{14}C. ^{14}C is radioactive. Silicon is the constituent of ceramics, glass and cement. Germanium present intraces. Tin present mainly as cassterite (SnO_2) and Lead as galena (PbS)

* Electron configuration : $ns^2 np^2$, n = 2 to 7

* Covalent radius : Increases down the group.

$_6C(77pm)$ $_{14}Si(118)$ $_{32}Ge$ (122) $_{50}Sn(140)$ $_{82}Pb146$ $_{114}Fl^*$

The small increase in care of Ge is due to inclusion of d-orbital and in Pb introduction of f-orbital. As d and f have less shielding effect the increased Z^* decreases the size out of greater attraction. So inspite of increased n-value shell no. the difference does not become significant.

* Ionisation Enthalpy : $\Delta iH^1_{(14)} > \Delta iH_1$ (group 13) in each period. The non sequential variation ΔiH value can be attributed to less shielding of d & f - electron. The increased Z^* increases the ΔiH value.

Ex. $\Delta iH_1(Pb) > \Delta_i H_1(Sn)$

$$[Xe]4f^{14}5d^{10}6s^2 6p^2$$

* Electronegativity : Greater than gr. 13 elements. Carbon is the most electronegative element of the group 2.5. The value Si–Pb are almost identical.

* Metallic behaviour : C and Si are non-metals. Ge is a metalloid, Sn and Pb are soft metals with low m.p. the m.p., of group 14 higher than those of group 13. The m.p. however decreases down the group. C(diamond) has the highest value of m.p. (4373K).

* **Oxidation states :**

Majority of the elements exhibits four oxidation state due to presence 4 unpair e^- in excited state.

e.g., $_6C^* = 1s^2 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$. The O.N. ranges from –4 to +4. The heavier elements exhibit +2 and +4 O.N., +2 state is more stable as sthe s^2 electron reluctant to take part in bonding process. The non participation of pair of electron, $\boxed{\uparrow\downarrow}$ is known as **inert pair effect**. Thus, Sn^{2+} stanous and Pb^{2+} (Plumbous) exist as stable ions & more common than Sn^{4+} and Pb^{4+} ions. Sn^{4+} and Pb^{4+} form covalent compounds as per Fajan rule.

* **Chemical properties :**

→ **Hydrides :** The stability of hydrides decreases from C to Pb. Carbon forms a wide varity of hybrides, alkane, C_nH_{2n+2}, alkene, CnH_2n and alkyne CnH_{2n-2}. Silicon hydride called silane, SiH_4, Si_2H_6 etc. Germanes are similar to silane. SnH_4(stanane) and PbH_4 (Plumbane) are only hydride of sn and Pb and they are difficult to prepare.

→ **Oxides :** Types : MO and MO_2. Oxides at higher 0.S. of elements are generally more acidic than those with lower O.S., CO_2, SiO_2 and GeO_2 are acidic while SnO_2 and PbO_2 are amphoteric. CO is neutral. Geo is distinctly acidic wheres SnO and PbO are amphoteric.

→ **Halides :** All form tetrahalide, MX_4, covalent and tetrahedral. Stability of tetrahalide decreases. Except halide of C, others undergo hydrolysis (due to presence of vacant d-orbitals)

$$\underset{\text{acid}}{SiCl_4} + \underset{\text{base}}{4H_2O} \longrightarrow Si(OH)_4 + 4HCl$$

In presence of excess acid complex anions are formed with six coordination number except C (due to absence of d-orbitals)

$$SiF_4 + 2F^- \longrightarrow [SiF_6]^{2-}$$

$$GeCl_4 + 2Cl^- \longrightarrow [GeCl_6]^{2-}$$

C di halide is highly unstable where $SnCl_2$ and $PbCl_2$ are quite stable. $PbCl_4$ is more stable than PbI_4.

As I^- can be easily oxidised liberating iodine.

$$PbI_4 \rightarrow PbI_2 + I_2$$

* **Anomalous behaviour of carbon.**

(i) Smaller size and high electro-vity, high ΔiH value.

(ii) It has maximum O.N. +4 and minimum –4.

Other element can have maximum covalency-6. e.g. $[SiF_6]^{2-}$

(iii) It fails to form complex due to absence of d-orbitals. ($c=1s^2\ 2s^2\ 2p^2$)

(iv) Due to smaller size it can form multiple bond i.e. $p_\pi p_\pi$ bond.

C = C, $C \equiv C$, C = O, C = S, $C \equiv N$.

(v) Catension . (Self linking property) This is due to greater strength of C – C bonds. The catenation decreases down the group. C>>Si > Ge = Sn. Pb does not show catenation.

Due to property of catenation and $p_\pi p_\pi$ bond formation, carbon is able to show allotropic form and a large number of compounds known.

* **Allotropess of carbon**. If an element exhibit, in different forms with varying physical properties but of identical chemical properties these are called allotropes (crystallice and amorphous)

Crystalline form - diamond, graphite, Fullerene

Amorphons form - charrcoal, coke, Lamp black, gas carbon etc.

→ Diamond (one carat = 0.2054 g) Cullinan the largest diamond (3026 carat). Here C undergoes sp^3 hybridisation producing a rigid three dimensional net work of C-atoms. Each C is bonded to 4C atoms tetrahedrally. C–C bond length 154 pm. It is the hardest substance as C–C bond enthalpy, 348 kJ/mol and hence used as abrassive for sharpening hard tools.

→ Graphite . Diamond + $O_2 \xrightarrow{1180K} CO_2$, no residue is left indicating it's pure form of carbon.

It has layer structure with planar hexagonal rings where each 'C' undergoes sp^2 hybridisation. C–C bond length in a ring is 141.5 pm and subsequent inter layer disttance is 340 pm. as such the layers are held by vander waals force. hence soft slippery and used as lubricant. $\underbrace{\boxed{1}\boxed{1}\boxed{1}}\boxed{1}$ The 4th $\bar{e}$ is delocalised over whole sheet hence it conducts electricity.

graphite $\xrightarrow{\text{Conc. } HNO_3}$ yellowish green graphitic acid, $C_{11}H_{15}O_5$.

→ Fullerene (1985) C_{60}, C_{70} Fullerenes are only the purest form of carbon because they have smooth structure without having dangling bonds. These are cage like molecules. C_{60} molecule has a shape like soccer (foot) ball called Buckminsterfullerene.It contains 20 six membered ring sand 12 five membered rings.A six membered ring is fused with five or six membered ring but a five membred ring can only fuse with six membered rings. All the C. atoms are equal & sp^2 hybridised i.e., C is attached to other 3–C atoms by σ . bonds. The 4th $\bar{e}$ gets delocalised in molecular orbitals providing it aromatic character.

$\Delta_f H$ of graphite = 0, diamond = 1.9, fullerence, C_{60} = 38.1 kJ/mol. Showing that graphite is thermodynamically more stable.

→ **Preparation :** Carbon was vaporised in an intense laser beam on graphite surface & then cooled in an inert stmosphere of helium to form cluster of C (C_{60} & C_{70})

→ Uses : (i) Fullerides used as semiconductor & super conductors.

(ii) Radio active isotopes being trapped / encapsulated inside fullerene can be used in cancer therapy and AIDS therapy.

* **Some important compounds of carbon and silicon.**

→ Carbon monoxide :

$$C_{(s)} + \frac{1}{2}O_2(g) \longrightarrow CO \text{ (in limited sypply of Oxygen)}$$

$$HCOOH \xrightarrow[\text{Conc.}H_2SO_4]{373K} CO$$

$$C_{(s)} + \text{steam}, H_2O \xrightarrow{1273} \xrightarrow[\text{water gas}]{CO_{(g)}+H_{2(g)}}$$

$$2C_{(s)} + \text{air}(O_2 + 4N_2) \xrightarrow{1273\ K} \underbrace{2CO_{(g)} + 4N_{2(g)}}_{\text{producer gas}}$$

* metal with CO form metal carbonyl. It complexes with haemoglobin to form carboxy haemoglobin (very stable complex) as a result the oxygen carrying capacity of blood gets reduced causing death.

* CO used in extraction different metals e.g. Ni by Mond's process.

* It is a powerful reducing agent:

$$Fe_2O_3(s) + 3CO_{(g)} \xrightarrow{\Delta} 2Fe(s) + 3CO_2 \text{ (Blast furnace)}$$

$$ZnO_{(s)} + CO_{(g)} \longrightarrow Zn(s) + CO_2$$

→ Carbon dioxide. $\bar{O} - C \equiv \overset{+}{O} \leftrightarrow O = O = O \leftrightarrow \overset{+}{O} \equiv C - \overset{-}{O}$

C – O bonds are identical (=115 pm), Non polar.

* Preparation : Coombustion of C & hydrocarbon (fuels)

$$C_{(s)} + O_{2(g)} \xrightarrow{\Delta} CO_{2(g)}$$

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O_{(g)}$$

$$CaCO_{3(s)} \xrightarrow[\Delta]{} CaO_{(s)} + CO_{2(g)} \text{ commercial scale)}$$

$$CaCO_{3(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O$$

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

* $H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$$

The H_2CO_3/HCO_3^- buffer system helps to maintain pH of blood between 7.26 to 7.42.

* Photosynthesis

* Excess CO_2 leads to increase **green house effect.**

* Solid CO_2 is called dry ice used as refrigerant.

* Being heavy and non-supporter of combustion used as fire extinguisher. Fire by Mg can't be extinguished as $CO_2 + 2Mg \longrightarrow 2MgO + C$

* Used in the synthesis of urea.

→ carbides : ionic (Al_4C_3), covaleent (CH_4, CCl_4, CS_2...), Interstitial carbide (TiC, ZrC etc.

→ Silicon dioxide, SiO_2 (95% of earth crust)

Polymorphous of SiO_2 (silica) : Quartz, cristobalite and tridymite.

SiO_2 is a solid (covalent) due to threedimensional polymeric net work where each Si is tetrahedrally bonded to four 'O' atoms.

- Use : To manufacturer glass . Glass & silica attached by HF only.

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

$$SiO_2 + 2NaOH \longrightarrow \underset{\text{Sodiumsilicate}}{Na_2SiO_3} + H_2O$$

- Silicon carbide (Carborundum)

$$SiO_2 + 3C \xrightarrow{3000K} SiC + 2CO$$

electric furnace with C-electrode

It is unaffected by acid but with NaOH in presence of air it forms silicate.

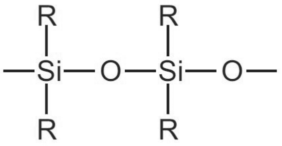
$$SiC + 2NaOH + 2O_2 \longrightarrow Na_2SiO_3 + CO_2 + H_2O$$

$$SiC + 2Cl_2 \longrightarrow SiCl_4 + C$$

- Used as abrassive, semiconductor, container for fuel elements in atomic reactor.
- Silicone : (Long chain organosilicon polymers, $-R_2SiO-$ as the repeating unit)
- Preparation- $Si + 2CH_3Cl \xrightarrow[\text{catalyst}]{Cu} (CH_3)_2SiCl_2$

$$\downarrow + 2H_2O$$

$$(CH_3)_2Si(OH)_2 + 2HCl$$



- $R\,SiCl_{3j}$ on hydrolysis forms Cross linked silicone.

* Uses : (i) silicone oil are used as grease, varnishes and resins
  (ii) Water repellants, good insulators
  (iii) Being bio-compatible used in surgical and cosmetic plants.

* Silicates : (feldspar, Zeolite, mica and asbestos)

Basic structural unit Si_4^{4-} (Orthosilicate)

$Si_2O_7^{6-}$ (Two tetrahedron) - pyrosilicate

$Si_3O_9^{6-}$ (Three SiO_4^{4-}) cyclic silicate

$(Si_6O_{18})^{12-}$ (six SiO_4^{4-}) chain silicates. The –ve charges get neutralised by cation e.g. $Be_3Al_2\,Si_6O_{18}$.

- main made silicates – glass and cement.

→ Zeolite : Here Al atoms replace few silicon atoms in three dimensional net work of silicon dioxide to give aluminosilicate acquiring –ve charge balanced by Na^+, K^+ or Ca^{2+}.

e.g. Feldspar an zeolite. ($Na\,Al\,SiO_4$). Zeolites are having honeycomb like stracture to act as molecular sleves

Uses : (i) For cracking of hydrocarbons.

(ii) Alcohol $\xrightarrow{ZSM-5}$ gasoline

(iii) Hydrated zeolites are used as ion exchange in softening hard water.

HOMEASSIGNMENT

(a) How does carbon differ from other elements of the group ?

(b) What are silicones ?

(c) Fill in the gaps :

  (i) Except Si and 'O' the atom present in zeolite is ___________ .
  (ii) A mixture ($CO+H_2$) is termed as ________ .
  (iii) C_{60} contains _____ no of six membered and _____ number of five members rings.
  (iv) The formula of quartz is _________ .
  (v) The chloride of group-14 which does not hydrolyse is ___________.

(d) Correct an rewrite the following sentences :

  (i) $SnCl_4$ is more covalent than $SnCl_2$.
  (ii) Dichlorocarbene is a stable molecule.
  (iii) In Fullenene C–undergoes sp^3- hybridisation.
  (iv) Potash alum is a complex salt.
  (v) Aluminium bronze contains Sn along with Al.

(e) Define $\Delta_i H$. Discuss its trend in group - 14.

L-92 - 93

UIIT - XII

ORGANIC CHEMISTRY (SOME BASIC PRINCIPLES AND TECHNIQUES

a) Definition : Compounds of carbon except

$CO, CO_2, CO_3^=, HCO_3^-, CN^-, NC^-, CNO^-, NCO^-$ and carbides of cotions where carbon usually combines with other element by covalente bond are called organic componds.

There fore , all organic compounds are compounds of carbon but all compounds of carbon are not organic compounds.

The number of organic compounds are very very vast- why?

i) One E.C of carbon is 2.4 . Inorder to satisfy its octet, it shares four of its outer most shell electrons with other elements forms four covalent bonds known as tetra valency of carbon. For the formation of covalent bond energy required is less which is available in nature . There fore , organic compound are widely distributed in plants and animals.

ii) The catanation (self combining capacity) of carbon is unique. Carbon can combine with itself in different manners to form Straight chain compounds, Branched chain compounds and Ring compounds.

b). Carbon is a peculier element and it undergoes sp , sp^2 and sp^3 hybridesation.

sp in $C \equiv C$, sp^2 in C=C, sp^3 in C-C(Refer hybridisation)

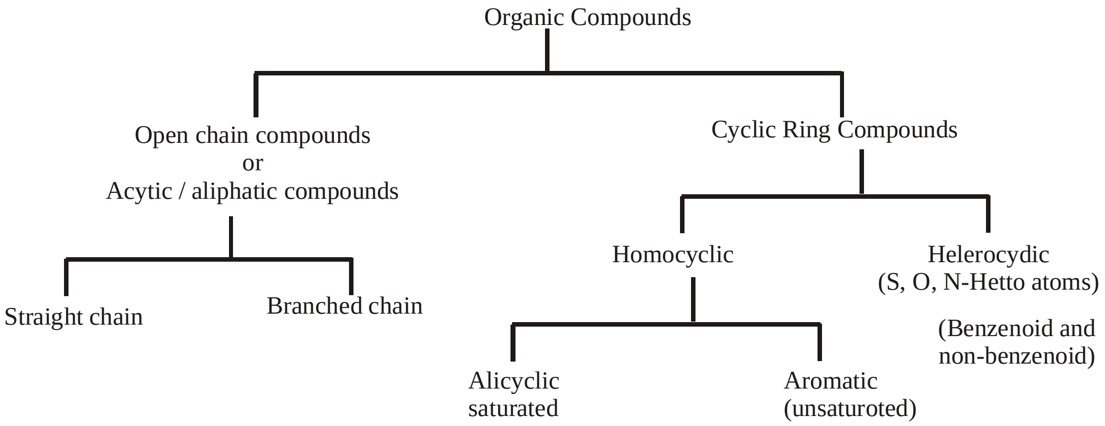
Sigma bond (σ) is formed due to maximum overlapping of electronic charge cloud. All single bonds are sigma bonds.

Pi bond (π) is formed due to minimum oerlapping of electronic charge cloud.

In a double bond, one bond is sigma (σ) and other are is Pi(π).

In a triple bond , one bond is sigma (σ) and other two are Pi(π).

c) Classification



d) Functional Group(F.G)

Functional group is either an atom or group of atoms or multiple bond (double bond/ triple bond) which decides the properties of a particular class of compound.

e) Homologous series ,

Compounds having same general formula , same functional group but adjacent differing by $-CH_2^-$ gropu or 14 mass unit are called homologous series.

For example , $CH_3OH, CH_3CH_2OH, CH_3CH_2CH_2OH......$ are homologous series of alcohol. Each member is called as homologue.

f) Nomenclature

Nomenclature of organic compounds are done according to International Union of Pure and applied chemistry (IUPAC) system. Accourding to this system an organic compound has these components (i) Name (ii) suffix or prefix or both (iii) Numerical number (if required)

Name:- Name of organic compound depends upon the number of carbon atom it contains-

No. of carbon atom	Name
1	meth
2	Eth
3	Prop
4	But
5	Pent
6	Hex
7	Hept
8	Oct
9	Non
10	Dec
11	Undec
12	Dodec

ii) Suffix/prefix or Both, depends upon the natre of the functional group it contains.

iii) Numerical number , is used when compunds have same molecular formula, same functional group but having different structre. The numerical number indicates the position of the functional group and it should be numerically lowest.

L-94, 95

a) Alkanes

General Formula (G.F) $\rightarrow$ CnH_{2n+2}

Functional group(F.G) - Alkans do not have any specific functional group , However , carbon carbon single bond is treated as F.G .

Suffix : -ane; N = 1, 2, 3,..........

Example

$N = 1, CH_4 \rightarrow \text{methane}$

$N = 2, CH_3CH_3 (C_2H_6) \rightarrow \text{Ethane}$

and son.

b) Alkene

G.F $\rightarrow$ CnH_{2n}

F.G $\rightarrow$ Carbon carbon double bond (C=C)

Suffix $\rightarrow$ -ene

n= 2, 3, 4...... $(n \neq 1)$

Examples

n = 2, $C_2H_4 \longrightarrow CH_2 = CH_2$ Ethene (Ethylene)

n = 3, $C_3H_6 \longrightarrow CH_3–CH=CH_2$ Propene

From butene on wards position of double bond to be indicated by numerical number which should be written in between the name and suffix and it should be numerically lowest.

n = 4, C_4H_8 (i) $CH_3CH_2CH = CH_2$
But -1-ene

(ii) $CH_3CH = CH – CH_3$
But-2-ene

and so on.

(c) Alkyne :

G.F. $\longrightarrow$ $C_nH_{2n–2}$

F.G. $\longrightarrow$ Carbon carbon triple covalent bond in the functional group $(C \equiv C)$

Suffix : $\rightarrow$ -yne

n = 2, 3, 4..... $(n \neq 1)$

Example :

n = 2, C_2H_2 ; $CH \equiv CH$, Ethyne (Acetylene)

n = 3, C_3H_4 ; $CH_3C \equiv CH$, Propyne

From butyne on wards numerical number is used to indicate the position of the triple bond and it should be numerically lowest and it is written in between name and suffix.

n = 4, C_4H_6 (i) $CH_3CH_2C \equiv CH$
But -1-yne

(ii) $CH_3\ C \equiv C - CH_3$

But-2-yne

(d) Alkyl group :

Alkane – H = Alkyl group / radical.

Alkyl group is symbolised by 'R'.

G.F. → $C_nH_{2n+1}^-$

n = 1, 2, 3 **,.........**

Naming : – ane of alkane is replaced by – y1.

n = 1, CH_3 – Methyl-

n = 2, C_2H_5 – or CH_3–CH_2 – Ethyl- and so on.

(e) Monohalogen derivative of saturated hydrocarbon or Alkyl halide (RX)

G.F. → C_nH_{2n+1} X or RX

Where X → F / Cl / Br / I

F.G. → X (F / Cl / Br / I)

n = 1, 2, 3,.......

Prefix → Halo (Fluoro / Chloro / Bromo/ Iodo)

Suffix → -ane

Example :

n = 1, X = Cl; CH_3Cl → Chloromethane (methyl chloride)

n = 2, X = Br, C_2H_5 Br Bromo ethane.

When n = 3, position of the F.G. is to be indicated by using numerical number which should be lowest.

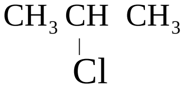
" The numerical number is written prior to the name of the compounds for which the functional group in written as prefix."

n = 3, x = Cl, C_3H_5Cl

(i) $CH_3CH_2\ CH_2\ Cl$

1 -chloropropane (propyl chloride)

(ii)



$CH_3\ \underset{\underset{Cl}{|}}{CH}\ CH_3$

2-chloropropane

(Isopropyl chloride)

and so on.

(f) Ether

G.B. → R–O–R/

Where R and R/ may be same or different alkyl groups.

F.G. → Etherial oxygen atom.

" Ethrical oxygen atom is one whose two valencies are satisfied by two different carbon atoms".

n = 2, 3, 4...........

Prefix → Alkoxy (Alkyl + oxygen = Alkoxy)

" The alkoxy group is formed when oxygen combines with the alkyl group having less carbon atom".

Sufix → – ane

Examples :

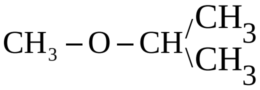
(i) $CH_3 - O - CH_3$ Methoxy methane (dimethyl ether)

(ii) $CH_3 - CH_2 - O - CH_2CH_3$ Ethoxyethane (Diethyl ether/ Ether)

“When one of the alkyl groups contain three or more carbon atoms, the numerical number is used and it is written prior to the name of the compound and it should be numerically lowest”.

Example ;

(i) $CH_3 - O - CH_2\ CH_2\ CH_3$
1– Methoxypropane

(ii) 
$CH_3 - O - CH\begin{matrix} / CH_3 \\ \backslash CH_3 \end{matrix}$ 2-Methoxypropane .

(g) Alcohol :

G. F. ⟶ $C_nH_{2n+1}OH$ or R OH

F.G. ⟶ –OH

n = 1, 2, 3, ...

suffix : ⟶ ‘e’ – of alkane in replaced by – o1. Alkane (–)e (+) pl → Alkanol

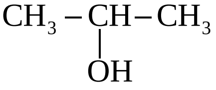
Example :

n = 1,	CH_3OH	Methanol	(Methyl alcohol)
n = 2,	CH_3CH_2OH	Ethanol (Ethyl alcohol or alcohol)	

“ Numerical number in used when alcohol possess three or more carbon atoms. The numerical number may be used either prior to the name or before the suffix or after the name but it should be numerically lowest”.

Example :

(i) $CH_3\ CH_2\ CH_2\ OH$
Propan-1-ol (Propyl alcohol)

(ii) 
$CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$

propan - 2- ol (Isopropyl alcohol).

L-96 and 97

(a) Aldehyde

G.F. ⟶ RCHO; where R is alkyl group or may be ‘H’ (Exception).

F.G. ⟶ –CHO

n = 1, 2, 3, ...

Suffix → ‘e’ of –ane of alkane is replaced by –al. (Alkanal)

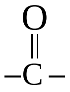
Example :

n = 1, HCHO Methanal (formaldehyde)

n = 2, CH_3 CHO Ethanal (Actaldehyde) and so on.

(b) Ketone -

G.F. → R–CO–R’, where and R’ may be same or different alkyl groups (but never Hydrogen).

F.G. → 
$-\overset{\overset{\displaystyle O}{\|}}{C}-$

n = 3, 4, 5........

Suffix → ‘e’ of –ane of alkane is replaced by –one.

Example :

n = 3, $CH_3\ COCH_3$ propanone (Acetone)

n = 4, $CH_3COCH_2CH_3$ Butanone

" Numerical number is used when 'n' becomes 5 and on wards, the numerical number indicates which carbon atom in the chain is carbonyl group and it should be numerically lowest".

Example :

(i) $CH_3COCH_2CH_2CH_3$

Pentan-2-one

(c) Carboxylic Acid

G.F. - RCOOH; Where 'R' is alkyl group or may be 'H' (Exception)

F.G. → – COOH

n = 1, 2, 3, ...

Suffix → 'e' of –ane of alkane is replaced by –oic acid. (Alkanoic acid)

Example :

n = 1, HCOOH Methanoic acid (formic acid)

n = 2, CH_3COOH Ethanoic acid (Acetic acid)

n = 3, CH_3CH_2COOH propanic acid and so on.

(d) Acid derivatives

(i) Acid halide

G. F. → R COX, where R → alkyl gr/H

X → F/Cl/Br/I

F.G. → – COX.

n = 1, 2, 3..........

Suffix → 'e' of – ane of alkane is replaced by –oyl halide.

Example :

n = 1 , X = Cl, HCOCl Methanoyl chloride.

n = 2, X = Br, CH_3COBr Ethanoyl bromide and so on.

(ii) Acid amide

G.F. → $RCONH_2$; where R = alkyl group/H.

F.G. → $–CONH_2$

n = 1, 2, 3......

Suffix → 'e' of – are of alkane is replaced by amide.

Example :

n = 1, $HCONH_3$ Methanamide

n = 2, CH_3CONH_2 Ethanamide and so on.

(iii) **Ester**

G.F. → RCOOR'; where R is alkyl group but R' cannot be 'H' and it is always an alkyl group.

F.G. → –COOR'

n = 2, 3, 4 ....

Prefix → alkyl according to R'

Suffix → 'e' of – are of alkane is replaced by – ate. (–alkanoate)

Example :

n = 2, $HCOOCH_3$ methyl methanoate

n = 3, CH_3COOCH_3 Methylethanoate

or $HCOOCH_2CH_3$ Ethyl methanoate

and so on.

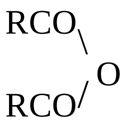
* Metallic derivatives of carboxylic acids are also named as enter.
HCOONa sodium methanoate.

(iv) Acid anhydride

Acid anhydrides are of two types.

(A) Same acids.

G.F. →

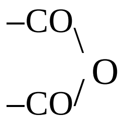


$$\begin{array}{l} RCO\backslash \\ \qquad\quad O \\ RCO/ \end{array}$$

or R–CO – O – CO – R

where R = alkyl gr/H

F.G. →



$$\begin{array}{l} -CO\backslash \\ \qquad\quad O \\ -CO/ \end{array}$$

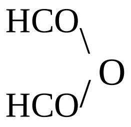
or – CO – O – CO –

n = 2, 4, 6, 8 .... (even nos)

Suffix : – 'e' of –are of alkane is replaced by – oic anhydride.

Examples :

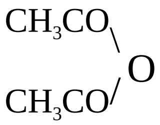
n = 2,



$$\begin{array}{l} HCO\backslash \\ \qquad\quad O \\ HCO/ \end{array}$$

methanoic anhydride

n = 4.

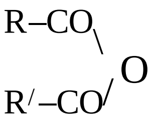


$$\begin{array}{l} CH_3CO\backslash \\ \qquad\qquad O \\ CH_3CO/ \end{array}$$

Ethanoic anhydride

(B) Different acids

G.B. →

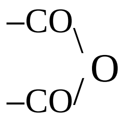


$$\begin{array}{l} R-CO\backslash \\ \qquad\qquad O \\ R'-CO/ \end{array}$$

or R – CO – O – R

R & R' are different alkyl groups and are of than may be 'H'.

F.G. → CO – O – CO or



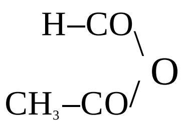
$$\begin{array}{l} -CO\backslash \\ \qquad\quad O \\ -CO/ \end{array}$$

n = 3, 4, 5 ....

Suffix : 'e' of –are of alkane is replaced by –oicanhydride but since the alkyl groups are different, the should be written in alphabatical order.

Example :

(i)

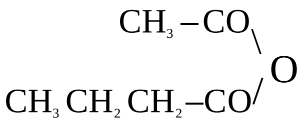


$$\begin{array}{l} \qquad H-CO\backslash \\ \qquad\qquad\qquad O \\ CH_3-CO/ \end{array}$$

or H – CO – O – CO – CH_3

Ethanoic methanoic anhydride.

(ii)



$$\begin{array}{l} \qquad\qquad CH_3-CO\backslash \\ \qquad\qquad\qquad\qquad\quad O \\ CH_3\,CH_2\,CH_2-CO/ \end{array}$$

Butanoic ethanoic anhydride.

(e) Compounds containing nitrogen

(i) **Nitro alkane**

G. F. : $C_nH_{2n+1}\ NO_2$

F.G. → $-NO_2$

n = 1, 2, 3 ....

Prefix → Nitro

Suffix → – ane (Saturated nitro compounds)

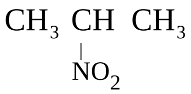
Example :

(i) $CH_3\ NO_2$ nitromethane

(ii) $CH_3VH_2NO_2$ nitroethane

" Numerical number is used when 'n' value becomes 3 or more".

$CH_3\ CH_2\ CH_2\ NO_2$ 1-nitro propane



$CH_3\ \underset{\substack{|\\NO_2}}{CH}\ CH_3$ 2- nitro propane

(ii) Alkane nitrite

G.F. → $C_nH_{2n+1}CN$

F.G. → CN

n = 2, 3, ...

Suffix – nitrile word is used after alkane counting all the 'C' atoms.

Examples :

(i) $CH_3\ CN$ Ethanenitrile (methyl cyanide)

(ii) CH_3CH_2CN Propanenitrile (Ethyl cyamide)

(iii) Amines are of three types.

Primary amine

G. F. → $C_nH_{2n+1}NH_2$

F.G → $-NH_2$

n = 1, 2, 3...............

Suffix : – 'e' of -are of alkane is replaced by – amine

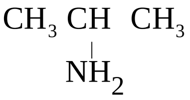
Example :

(i) CH_3NH_2 Methanamine

(ii) $CH_3\ CH_2\ NH_2$ Ethanamine

" Numerical number is used when 'n' becomes 3 or more".

$CH_3\ CH_2\ CH_2\ NH_2$ Propan-1-amine.



$CH_3\ \underset{\substack{|\\NH_2}}{CH}\ CH_3$ propan-2-amine

(B) Secondary amine

G. F. → $C_nH_{2n+1}NHR^{/}$

$R^{/}$ must be an alkyl group

F.G → $-\ NHR^{/}$

n = 2, 3, 4 ....

Prefix →– N – alkyl

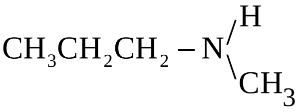
Suffix → **‘e’** of – are of alkane is replaced by -amine.

Examples :

(i) $CH_3\ NH - CH_3$
N-methyl methanamine

(ii) $CH_3\ CH_2\ NH\ CH_3$
N-methyl ethanamine

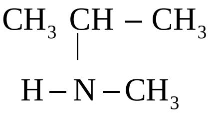
(iii)



$$CH_3CH_2CH_2-N\begin{array}{l}\diagup H\\ \diagdown CH_3\end{array}$$

N-methyl propan - 1 - amine

(iv)

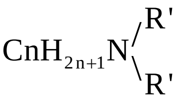


$$\begin{array}{l}CH_3\ \underset{|}{CH}-CH_3\\ \quad H-N-CH_3\end{array}$$

N-methyl propan-2-amine

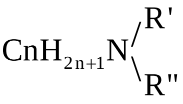
(C) Tertiary amine

G. F. ⟶



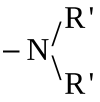
$$CnH_{2n+1}N\begin{array}{l}\diagup R'\\ \diagdown R'\end{array}$$

or



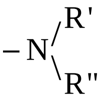
$$CnH_{2n+1}N\begin{array}{l}\diagup R'\\ \diagdown R''\end{array}$$

F. G. ⟶



$$-N\begin{array}{l}\diagup R'\\ \diagdown R'\end{array}$$

or



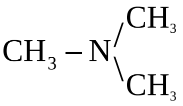
$$-N\begin{array}{l}\diagup R'\\ \diagdown R''\end{array}$$

Prefix ⟶ N, N – dialkyl or N - alkyl – N – alkyl in alphabatical order.

Suffix –’e’ of –are of alkane in replaced by - amine.

Examples

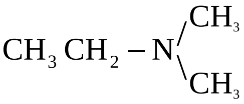
(i)



$$CH_3-N\begin{array}{l}\diagup CH_3\\ \diagdown CH_3\end{array}$$

N, N-dimethylmethanamine.

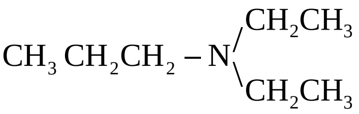
(ii)



$$CH_3\ CH_2-N\begin{array}{l}\diagup CH_3\\ \diagdown CH_3\end{array}$$

N, N - dimethylethanamine.

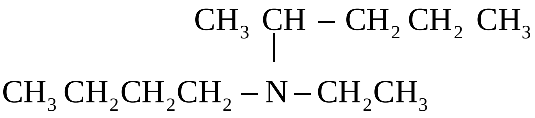
(iii)



$$CH_3\ CH_2CH_2-N\begin{array}{l}\diagup CH_2CH_3\\ \diagdown CH_2CH_3\end{array}$$

N, N - diethylpropan-1-amine

(iv)



$$\begin{array}{l}\qquad\qquad\qquad CH_3\ \underset{|}{CH}-CH_2\,CH_2\ CH_3\\ CH_3\ CH_2CH_2CH_2-N-CH_2CH_3\end{array}$$

N-butyl - N - ethyl pentan-2-amine.

Parent amine must contain none C-atoms in chain.

L-98, 99, 100

IUPAC - Rules for naming complicated branched chain alkanes.

1. Longest chain Rule :

(a) Select the longest continuous carbon chain which is called the parent chain and it bears the name of the compound. The longest continuous carbon chain is not necessarily a straight chain. The carbon chains which are not included in the parent chain are called as side chains or substituent.

(b) In case of a compound having more than one carbon chain of maximum number of carbon atom, the chain having more number of side chains is selected on the parent chain.

2. Numbering of the carbon chain :

The longest continuous carbon chain (parent chain) is then numbered by using arabic numerals like 1, 2, 3, 4....... etc from one end to other such that carbon atom having the substituent should get a lowest possible number. The numerical number that indicates the position of the substituent is called its LOCANT.

3. Lowest set Rule :

When a compound contain two or more substituents, the longest continuous carbon chain (parent chain) is then so numbered that the numerical number used to locate the psitions of the substituents should get a lowest set when compared one by one.

(This rule superceeds the lowest sum rule).

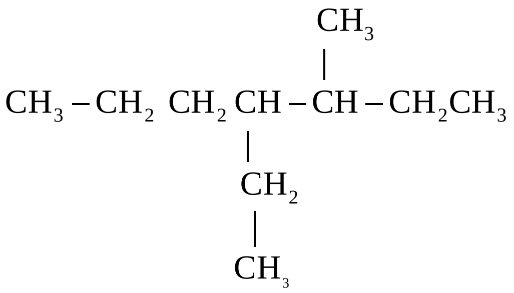
4. The name of the substituent is written as prefix preeceded by its locant to the name of the parent hydrocarbon. A hyphen **but not a coma** separates the locant from the name of the substituent.

5. If two or more substituents are present then they are written in alphabatical order preceeded by their locants.

6. If the same substituents is repeated for two or more times, a prefix of di-, tritetra- etc are used to the name of the substituents. (The word di-, tri-, tetra etc. are called multiplying prefixes). Its locants are written in the increasing numerical order separated by coma among itself followed by a hyphen to the name of the substituent. The multiplying prefixen like di-, tri-, tetra - etc. are of being used to decide the alphabatical order of the substituents.

Examples :

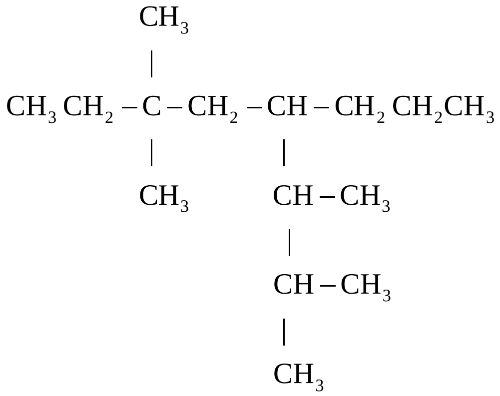
1.



$$CH_3-CH_2\ CH_2\ \underset{\underset{\underset{\underset{CH_3}{|}}{CH_2}}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_2CH_3$$

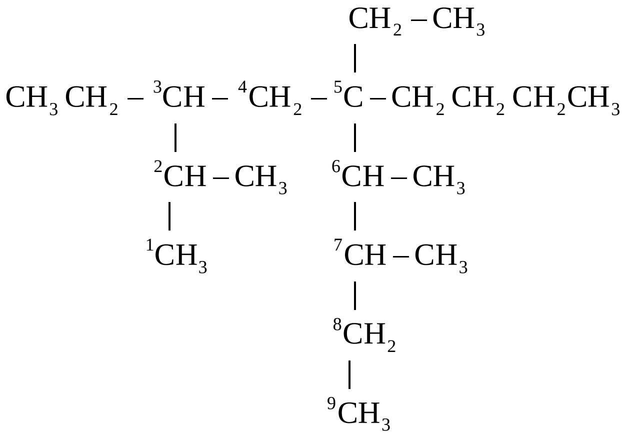
4-ethyl-3-methyl heptane

2.



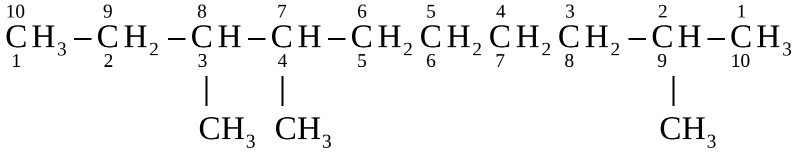
2, 3, 6, 6, – tetramethul - 4 - propyl octane

3.



5 - butyl - 3, 5 - diethyl - 2, 6, 7-trimethyl nonane.

4.



$$\overset{10}{\underset{1}{C}}H_3-\overset{9}{\underset{2}{C}}H_2-\underset{\underset{CH_3}{|}}{\overset{8}{\underset{3}{C}}H}-\underset{\underset{CH_3}{|}}{\overset{7}{\underset{4}{C}}H}-\overset{6}{\underset{5}{C}}H_2\overset{5}{\underset{6}{C}}H_2\overset{4}{\underset{7}{C}}H_2\overset{3}{\underset{8}{C}}H_2-\underset{\underset{CH_3}{|}}{\overset{2}{\underset{9}{C}}H}-\overset{1}{\underset{10}{C}}H_3$$

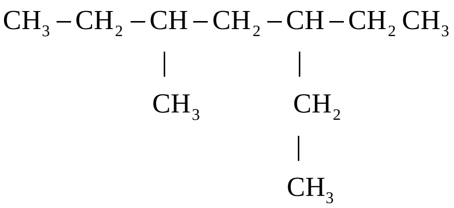
2, 7, 8 - trimethyl decane.

From right 2, 7, 8 (Locont comes first)

From left. 3, 4, 9

7. Naming different substituent, at equivalent positions i.e., having equal sets.

If two different substituent, are in equivalent positions from the two ends of the chain (two sets of locants are equal), then the numbering of the carbon chain is done in such a way that the substituent which comes first in the alphabatical order should get lower number.

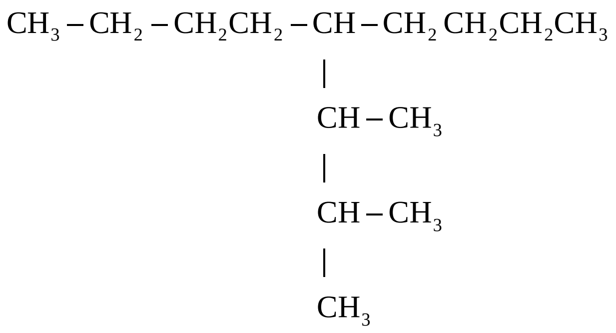


$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\begin{array}{c}|\\CH_2\\|\\CH_3\end{array}}{CH}-CH_2CH_3$$

3-ethyl-5-methyl heptane

8. Naming of the complex substituent

If the side chain is itself branched then it is written as substituted alkyl group within a bracket and its carbon atoms are counted from the carbon atom of the parent chain to which it is attached.



5-(1, 2- dimethyl propyl) nonane.

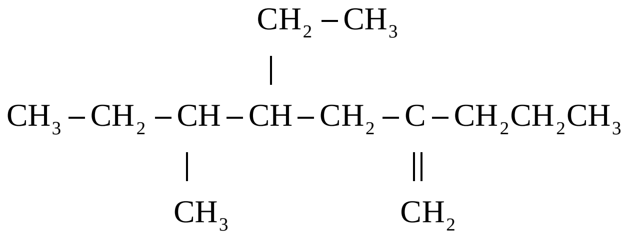
B. Compounds containing multiple bonds with branching.

(a) Compounds containing only one multiple bond with branching

1. Select the longest continuous carbon chain so as to include the multiple bond within the chain and in doing so it may not contain maximum number of carbon atoms.
2. The suffix of the compound is written as per the multiple bond it contains.
3. The longest continuous carbon chain having the multiple bond is then numbered in auch a way that the carbon atom containing the multiple bond should get the lowest possible number.
4. All the rules regarding writing of the substituents remain same as that for alkanes.

Examples :

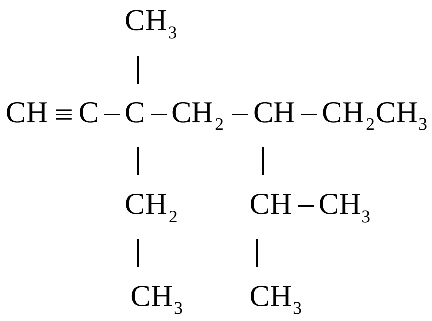
(i)



$$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle CH_2-CH_3}{\overset{|}{CH}}-CH_2-\underset{\displaystyle CH_2}{\underset{\|}{C}}-CH_2CH_2CH_3$$

4-ethyl-5-methyl-2-propylhept-1-ene

(ii)



3, 5-diethyl - 3, 6 - dimethylhept -1-yne

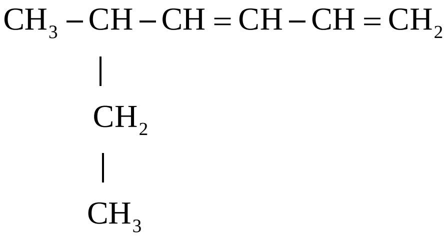
(b) Compounds containing more than one like multiple bonds.

In case of compounds containing more than one like multiple bonds, then the prefix di-, tri-, tetra– etc. are used either before – ene or –yne. The locants used to indicate the positions of the multiple bonds must be a lowest set.

Examples :

(i) $CH_2 = CH - CH = CH_2$ Buta-1, 3–diene

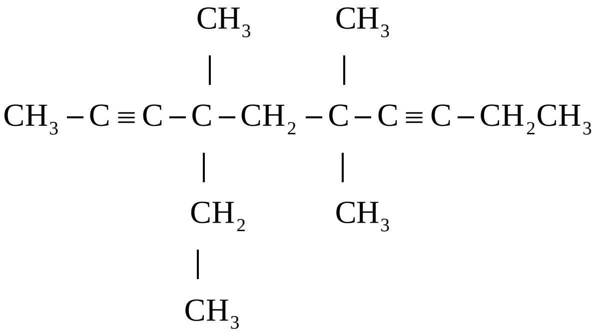
(ii)



$$CH_3 - \underset{\substack{|\\CH_2\\|\\CH_3}}{CH} - CH = CH - CH = CH_2$$

5-methyl hepta-1, 3=dienel

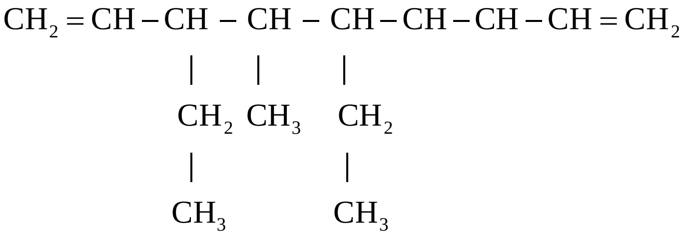
(iii)



$$CH_3 - C \equiv C - \underset{\substack{|\\CH_2\\|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}} - CH_2 - \underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}} - C \equiv C - CH_2CH_3$$

4-ethyl-4, 6, 6–trimethyl deca-2, 7-diyne.

(iv)



$$CH_2 = CH - \underset{\substack{|\\CH_2\\|\\CH_3}}{CH} - \underset{\substack{|\\CH_3}}{CH} - \underset{\substack{|\\CH_2\\|\\CH_3}}{CH} - CH - CH - CH = CH_2$$

5, 7 – diethyl-6-methyl nona-1, 3, 8-triple

(c) Compounds containing both double bond (s) and triple bond (s).

1. In case of a compounds containing both double bond and triple bond, the suffix ends with -yne preceded by its locant, prior to ene is written preceded by its locant.

2. The terminal 'e' of –ene (or -yne or -ane is dropped when it is followed by the suffix begining with a, i, o, u and y. The a, i, o **u and y are called organic vowels.**

3. Number as low as possible are given to double bond or triple bond as a set, even though this may at times give - yne a lower number than –ene. However, if a choice is there, preference for lower locant is given to double bond, but the family will be of –yne (i.e., end with –yne).

Examples

(i) $\overset{5}{C}H \equiv \overset{4}{C} - \overset{3}{C}H_2\ \overset{2}{C}H = \overset{1}{C}H_2$ pent-1-en-4-yne

(ii) $CH\equiv C-CH=CH-CH=CH_2$ Hexa-1, 3-din-5-yne

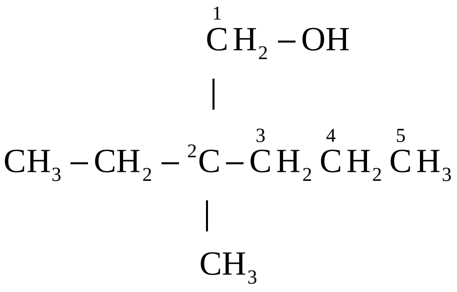
(iii) $H\overset{1}{C}\equiv\overset{2}{C}-\overset{3}{C}H=\overset{4}{C}H-\overset{5}{C}H_3$ Pent-3-2n-1-yne

C. Compounds containing one functional group and substituents

1. Select the longest continuous carbon chain containing the carbon atom having the functional group.
2. The suffix or prefix or both is written as per the functional group it contains.
3. The numbering of carbon atoms is done in such a way that the carbon atom having the functional group should get the lowest possible number. If the functional group contain carbon atom (except ketone), it is numbered as 1 and usually not mentioned.
4. All the rules regarding the writting of the substituents remain same as that of alkane.

Examples :

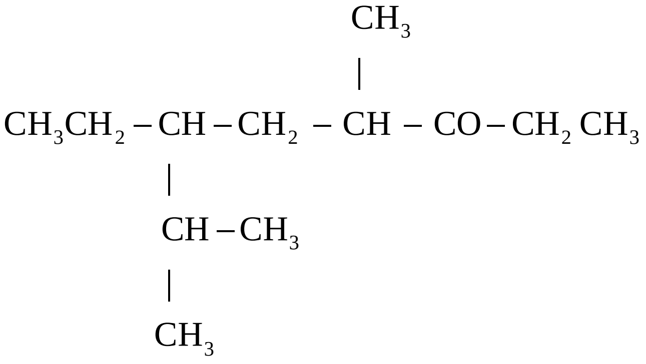
(i)



$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{\overset{1}{C}H_2-OH}{|}}{{}^2C}}-\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3$$

2-ethyl-2-methyl-pentan-1-ol

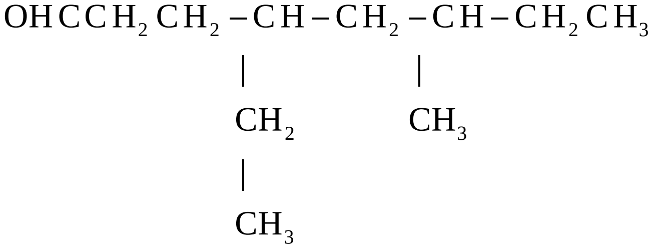
(ii)



$$CH_3CH_2-\underset{\underset{\underset{\underset{CH_3}{|}}{CH-CH_3}}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CO-CH_2CH_3$$

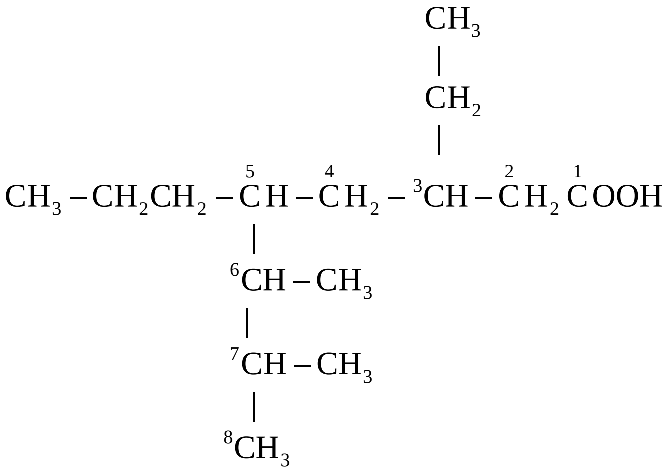
6-ethyl-4,7-dimethyl-3-octanon-3-one

(iii)



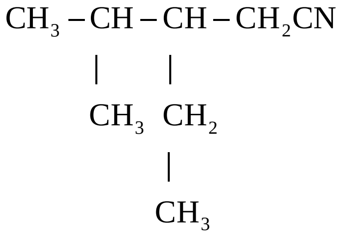
$$OH\overset{1}{C}\overset{2}{C}H_2\overset{3}{C}H_2-\underset{\underset{\underset{\underset{CH_3}{|}}{CH_2}}{|}}{\overset{4}{C}H}-\overset{5}{C}H_2-\underset{\underset{CH_3}{|}}{\overset{6}{C}H}-\overset{7}{C}H_2\overset{8}{C}H_3$$

4-ethyl-6-methyloctaanal

(iv) 

$$CH_3-CH_2CH_2-\underset{\begin{array}{l}|\\{}^{6}CH-CH_3\\|\\{}^{7}CH-CH_3\\|\\{}^{8}CH_3\end{array}}{\overset{5}{C}H}-\overset{4}{C}H_2-\overset{\begin{array}{c}CH_3\\|\\CH_2\\|\end{array}}{{}^{3}CH}-\overset{2}{C}H_2\overset{1}{C}OOH$$

3-ethyl-6-7- dimethyl-5-propyl octanoic acid.

(v) 

$$CH_3-\underset{\begin{array}{c}|\\CH_3\end{array}}{CH}-\underset{\begin{array}{c}|\\CH_2\\|\\CH_3\end{array}}{CH}-CH_2CN$$

3-ethyl-4-methyl pentanenitrile.

D. Compounds containing functional group, multiple bonds and substituents.

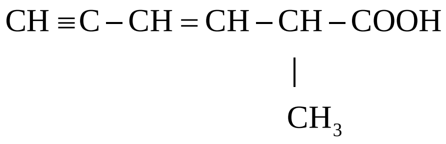
If the compound contains a functional group, multiple bond and side chains the order of preference for numbering is :

F.G. > = > $\equiv$ > substituents.

Examples :

(i) $CH_2=CH-CH_2\ COCH_3$ Pent-4-en-2-one

(ii) $CH_3CH = CH - CH_2 - OH$ But-2-en-1-ol But-2-en-1-ol

(iii) 

$$CH\equiv C-CH=CH-\underset{\begin{array}{c}|\\CH_3\end{array}}{CH}-COOH$$

2-methyl hex-3-en-5-ynoic acid.

E. Compounds containing two or more different functional groups

When an organic compound containing two or more different functional groups, one group is treated as the principal functional group and it bears the name. The other group(s) is regarded as the secondary functional group and is written as prefix.

The order for the preference of principal functional group and the names of the secondary functional groups which are written as prefix are as follows.

Functional group	**Prefix**
– COOH	Carboxy –
– COOR	alkoxy carbonyl –
– COX	haloformyl –
– $CONH_2$	carbamoyl –

– CN	cyano –
– CHO	formyl –
– C = O	Keto / oxo –
– OH	hydroxy–
– NH_2	amino–
– OR’	alkoxy –
– X	halo–

E. Compounds containing two or more like functional grups.

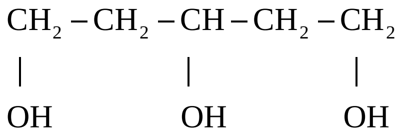
(a) If a compound contain two or more one like functional groups, then the multiplying prefix di-, tri-, tetra-etc are used before the name of the secondary suffix (–ane, –ene, –yne are called primary siffixes and the rest of the suffixes are called secondary suffixes). In this case the terminal ‘e’ of the primary suffix is retained while writting the name.

Examples :

(i) $OHC - CH_2\ CH_2\ CH_2 - CHO$
Pentanedial

(ii) HOOC – COOH ethane dioic acid

(iii) $NC - CH_2\ CH_2\ CN$ Butane dinitrile

(iv) 

$$\underset{\underset{OH}{|}}{CH_2} - CH_2 - \underset{\underset{OH}{|}}{CH} - CH_2 - \underset{\underset{OH}{|}}{CH_2}$$

Pentane - 1, 3, 5 – triol

(v) $CH_3 - CO - CH_2 - CO - CH_3$
Pentane-2, 4-dione.

L-101, 102, 103

Isomerism : The word isomerism is coined from two greek words. iso - same and mers - parts “Compounds having same molecular formula but having different structures, having different physical and chemical properties are called isomers and the phenomenon is known as isomerism. They are of two types : A . Structural isomerism

B. Stereo isomerism.

Structural isomerism.

“ Compounds having same molecular formula but differing in the arrangement of atoms / groups within the molecule, there by giving different structurees are called structural isomers and the phenomenon is knwn as structural isomerism. They are of five different types.

1. Chain isomerism
2. Position isomerism
3. Functional isomerism
4. Metamerism
5. Tautomerism.

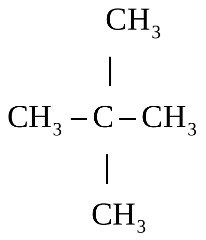
Chain isomerism

“ Compounds having same molecular formula but differing in the nature carbon chain are called chain isomers and the phenomenon is known as chain isomerism”.

Examples :

(a) $CH_3CH_2CH_2CH_3$ (Butane) and $CH_3–CH(CH_3)–CH_3$ (2-methyl propane)

(b) $CH_3\ CH_2\ CH_2\ CH_2\ CH_3$ n – pentane $CH_3-CH(CH_3)-CH_2-CH_3$ 2–methylbutane and



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$$

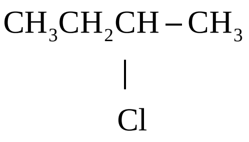
neo- pentane. (2, 2-dimethyl propane)

2. Position isomerism

"Compounds having same molecular formula having same functional group but differing in the position of the functional group are called position isomers and the phenomenon is known as position isomerism."

Example :

(a) $CH_3\ CH_2\ CH_2\ CH_2\ Cl$ 1 – chlorobutane and



$$CH_3CH_2\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_3$$

2-chlorobutane

(b) $CH_3\ CH_2\ CH = CH$ But-1-ene and $CH_3\ CH = CH - CH_3$ But-2-ene

3. Functional isomerism

"Compounds having same molecular formula but having different functional groups are called functional isomers and the phenomenon is known as functional isomerism."

Example :

(a) CH_3CH_2OH Ethanol and $CH_3 - O - CH_3$ Methoxy methane

(b) $CH_3\ CH_2\ CHO$ Propanal and $CH_3-CO-CH_3$ Propanone

(c) $CH_3\ CH_2COOH$ Propanoic acid and $CH_3\ COOCH_3$ Methyl ethanoate

4. Metamerism

" Compounds having same molecular formula, having same functional group but differing in the number of carbon atoms in the alkyl group an either side of the functional group are called metamers and the phenomenon is known as metamerism".

Example :

(a) $CH_3\ CH_2-O-CH_2CH_3$ Ethoxy ethane and $CH_3-O-CH_2CH_2CH_3$ 1 – methoxy propane

(b) $CH_3-NH-CH_2CH_2CH_3$ N – methyl propan – 1 – amine and

$CH_3-CH_2NH-CH_2CH_3$

N-ethyl ethanamine

5. Tautomerism

This is a special type of functional isomerism. when two compounds having same molecular formula but exist in dynamic equilibrium with each other are called tautomers and the phenomenon is known as tautomerism”.

Example :

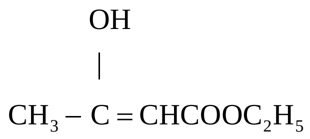
(a) $CH_3-C\equiv N \rightleftharpoons CH_3\overset{:\rightarrow}{N} = C \qquad (CH_3-\overset{+}{N}\equiv\overline{C})$

Methyl cyanide Methyl isocyamide

(b) $CH_3CHO \rightleftharpoons CH_2=CH-OH$

Acetaldehyde Vinyl alcohol

(c) $CH_3COCH_2COOC_2H_5 \rightleftharpoons$



$CH_3-\underset{}{\overset{\overset{\displaystyle OH}{|}}{C}}=CHCOOC_2H_5$

Keto form of acetoacetic ester Enol form of aceto acetic ester

Stereo Isomerism

“ Compounds having same molecular formula but differing in the spatial arrangement of atoms or groups within the molecule are called called stereo isomers and the phenomenon is known as stereo isomerism”. They are of two types.

(a) Configurational isomerism. (Stereos → occupying)

(b) conformational isomerism

Configurational isomerism are again of two types. They are

1. geometrical isomerism
2. Optical isomerism.

Geometrical isomerism

“ Compounds having same molecular formula but differing in the spatial arrangement of atoms or groups around a crabon-carbon double bond around carbon-nitrogen double bond are called geomtrical isomers and the phenomenon is known as geometrical isomerism.

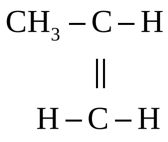
This is due to restriction of free rotation around C = C / C = N leading to two different geometry of the compound.

Conditions required :

1. The molecule must have a carbon - carbon double bond or carbon-nitrogen double bond.

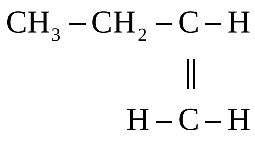
2. The atoms or groups attached to carbon atom having C = C or C = N must be different.

If are or both the carbon atoms having the double bond carry two similar atoms or groups, then no geometrical isomerism will be possible. For example, propene and but-1-ene does not exhibit geometrical isomerism.



$$\begin{array}{c} CH_3-C-H \\ \| \\ H-C-H \end{array}$$

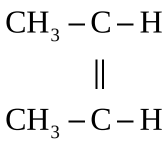
propene



$$\begin{array}{c} CH_3-CH_2-C-H \\ \| \\ H-C-H \end{array}$$

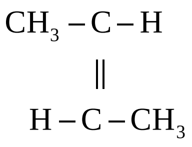
But – 1 – ene

However, but -2-ene exhibit geometrical isomerism.



$$\begin{array}{c} CH_3-C-H \\ \| \\ CH_3-C-H \end{array}$$

and



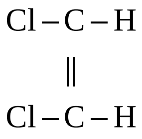
$$\begin{array}{c} CH_3-C-H \\ \| \\ H-C-CH_3 \end{array}$$

But-2-ene cis-form But-2-ene trans-form

(If two like groups are on the same side C=C, it is called cis-form and if opposite side of C=C, it is called trans-form).

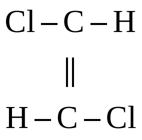
Other Examples :

(a)



$$\begin{array}{c} Cl-C-H \\ \| \\ Cl-C-H \end{array}$$

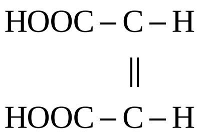
and



$$\begin{array}{c} Cl-C-H \\ \| \\ H-C-Cl \end{array}$$

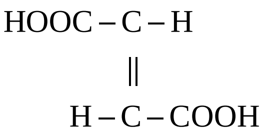
Cis-1, 2-dischloro ethene Trans-1,2-dichloro ethene

(b)



$$\begin{array}{c} HOOC-C-H \\ \| \\ HOOC-C-H \end{array}$$

and



$$\begin{array}{c} HOOC-C-H \\ \| \\ H-C-COOH \end{array}$$

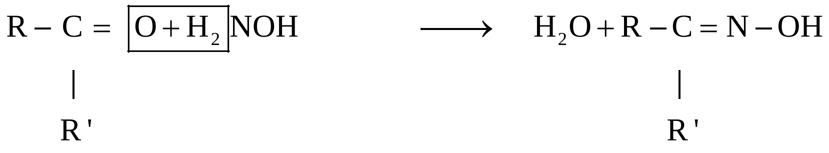
Cisform of but-2-ene dioicacid trans-form of but-2-ene dioic acid

(Maleic acid) (Fumeric acid)

When an aldehyde or ketone reacts with hydroxylamine, aldoxime and ketoxime are formed respectively.

$$\begin{array}{c} R-C=\boxed{O+H_2}NOH \\ | \\ H \end{array} \longrightarrow \begin{array}{c} H_2O+R-C=NOH \\ | \\ H \end{array}$$

Aldehyde Hydroxyl amine Aldoxime



$$\begin{array}{c} R-C=\boxed{O+H_2}NOH \\ | \\ R' \end{array} \longrightarrow \begin{array}{c} H_2O+R-C=N-OH \\ | \\ R' \end{array}$$

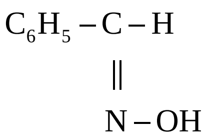
Ketone Hydroxyl amine Ketoxime

Aldoximes and ketoximes possess C = N

Aldoximes :

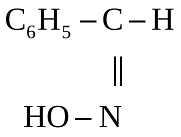
Whenthe isomer have ‘H’ and ‘OH’ another same side of C=N, it is called “syn” isomers and when they are opposite to C = N, it is called “anti” isomers.

Example :



$$\begin{array}{c} C_6H_5-C-H \\ \| \\ N-OH \end{array}$$

and



$$\begin{array}{c} C_6H_5-C-H \\ \| \\ HO-N \end{array}$$

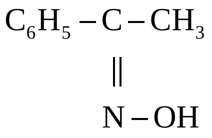
Syn-farm of Benzaldoxime (α -Benzaldoxime)

Syn-farm of Benzaldoxime (β -Benzaldoxime)

Ketoximes

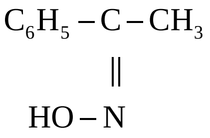
In case of keto-oxime, the ground which is pronounced first and 'OH' groups are on the same side of $C = N$, it is called 'syn' isomers "anti" isomer.

Example :



$$\begin{array}{c} C_6H_5-C-CH_3 \\ \| \\ N-OH \end{array}$$

and



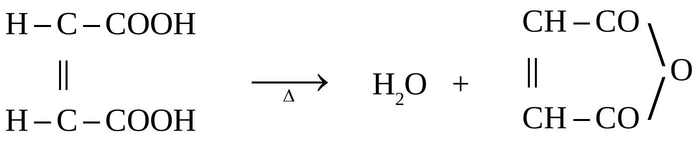
$$\begin{array}{c} C_6H_5-C-CH_3 \\ \| \\ HO-N \end{array}$$

Syn-form of methyl phenyl ketoxime

Anti-form of methyl phenyl ketoxime

Characteristics of geometrical isomers

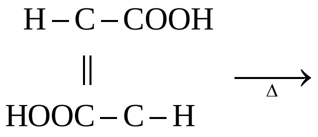
1. The geometrical isomers have got similar chemical properties, since they have same functional groups. However, the rate (speed) of the reaction is different. For example, when maleic acid is heated forma its anhydride easily but not fumeric acid.



$$\begin{array}{c} H-C-COOH \\ \| \\ H-C-COOH \end{array} \xrightarrow{\Delta} H_2O + \begin{array}{c} CH-CO \\ \| \\ CH-CO \end{array}\!\!\!> O$$

Maleicacid

Maleic anhydrid early formed since two – COOH grs. are on the side



$$\begin{array}{c} H-C-COOH \\ \| \\ HOOC-C-H \end{array} \xrightarrow{\Delta}$$

No anhydride is formed earily as two – COOH groups are on the opposite side of $C = C$

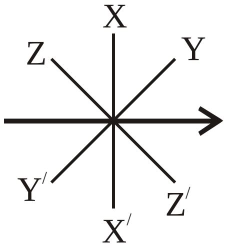
Fumeric acid

2. The geometrical isomers have different physical properties. This is due to the fact that the cis isomer is unsymmetrical and exist as a single molecule but the trans isomer is symmetrical and exist in cluster form.

	Ph. properties	Cis-form	Trans-form
(i)	Solubility	High	Low
(ii)	M.pt & B. pt	Low	High
(iii)	Dipole moment	Have +ve value	Zero or negligible
(iv)	Refractive index	High	Low

Optical Isomerism

" Compounds having same molecular formula, same physical & chemical properties but differing in their behaviour towards the plane of polarised light are called optical isomers and the phenomenon is known as optical isomerism".



Ordinary light :

In case of an ordinary light, the particle of the medium vibrate in infinite possible planes perpendicular to the line of propagation.

Polarised light

When an ordinary light is passed through a Nicol's prism, the vibration of particle in infinite planes are being cut off and is allowed to vibrate only in one possible plane perpendicular to the line of propagation. This uniplanner vibration of the particle perpendicular to the line of propagation of light is called the **polarised light.**

When an organic compound either in Liquid state or in solution state (must be transparent to light) is kept in the path of the plane of polarised light two things may be happened.

1. The plane of the polarised light is not rotated, then the organic compound is said to be **optically inactive.**
2. The plane of the polarised light is rotated from its original plane. (say $XX^{/}$), then the organic compound is said to be optically active.

   (i) If the plane of polarised light is rotated in clockwise direction i.e., towards right of the original plane (from $xx^{/}$ to $yy^{/}$ plane). Then the orgnaic compound is said to be dextro-rotatory form or d-form of the compound.

   (ii) If the plane of polarised light is rotated in an anticlockwise direction or toward left of the original plane (from xx' to zz' plane), then the organic compound is said to be laevorotatory form or l-form of the compound.

(The above experiment is carried out in an instrument known as polarimeter)

The angle between the original plane and the newplane of the polarised light is called "observed angle of rotation" and it is symbollised as '$\propto$'.

The observed angle of rotation $(\propto)$ depends upon the following factors.

1. Nature of the compound.
2. Nature of the solvent used
3. Temperature
4. Wave length of the light used
5. Concentration of the solution
6. Length of the solution i.e., the length of the tube used to keep the solution.

Angle of specific rotation.

For the measurement of optical rotation, a term specific rotation or angle of specific rotation is used. This is a physical constant and characteristic of an organic compound like m.pt, b.pt. density, refractive index etc. it is written as:

$$[\propto]_{D}^{t^{o}} = \frac{\alpha_{obs}}{\ell \times C}$$

Where t $\rightarrow$ temp, $D \rightarrow 'D'$ line of Na.

$\alpha - obs \longrightarrow$ observed angle of rotation.

$\ell \longrightarrow$ length of the solution ie., length of the tube in decimeter.

$C \longrightarrow$ concentration of the solution in gm/ml.

Thus, “the angle of specific rotation may be defined as the observed angle of rotation when concentration of the solution is 1 g/ml and the length of the tube is 1 decimeter”.

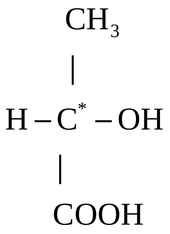
Requirement.

In order to be optically active an organic compound must posses the followings :

1. It must possess one or more a symmetric carbon atom or chiral carbon atom.

“ Asymmetric carbon atom or chiral carbon atom is one, whose four valencies are satisfied by four different atoms or groups”.

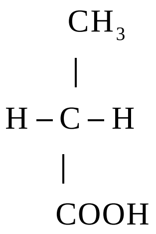
Example :



$$\begin{array}{c} CH_3 \\ | \\ H-C^{*}-OH \\ | \\ COOH \end{array}$$

* marked ‘C’ atom is the an asymmetric carbon atom

Lactic acid
2-hydroxy propanoic acid.
(It is optically active)



$$\begin{array}{c} CH_3 \\ | \\ H-C-H \\ | \\ COOH \end{array}$$

But, propanoic acid has no asymmetric carbon atom and hence it is not optically active.

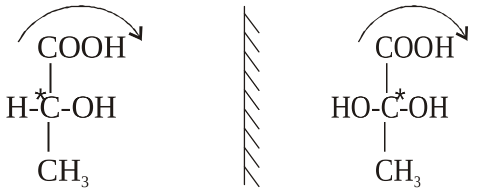
The number of isomers formed depebds upon the number of a symmetric carbon atom present in an organic compound. If the no. of asymmetric carbon atom present an organic compound is then the no of asymetric carbon atom is present ‘n’ the number of isomers formed is 2^n.

2. The molecule as a whole should be an asymmetric one i.e., should not possess a plane of symmetry. For example a ball has a plane of symmetry but a tree does not have a plane of symmetry.

Optical isomerism of compounds having one asymmetric carbon atom.

Example : 2-hydroxy propanoic acid or Lactic acid.

Since the compound possess are asymmetric carbon atom, the number of isomers formed by it is , $2^n = 2^1 = 2$, they are:



$H-\overset{\overset{COOH}{|}}{\underset{\underset{CH_3}{|}}{\overset{*}{C}}}-OH$ $\qquad$ $HO-\overset{\overset{COOH}{|}}{\underset{\underset{CH_3}{|}}{\overset{*}{C}}}-OH$

(mirror image not super imposable)

I **II**

Out two atructures, I & II, one of them rotate the plane of polarised light in clockwise direction and other in anticlockwise direction. Therefore, ore of them is d-form and other one is ℓ -farm. These are called a pair of enantiomers.

Properties of Enantiomers.

1. They are mirror image of each other.
2. They are not super imposible.
3. They have same physical and chemical properties.
4. They rotate the plane of polarised light to the same extent but in opposite direction.

Racemic mixture

" The equimolar mixture of d-form and *l*-forn of a compound resulting in the formation of an optically inactive mixture is called **racemic mixture**". Racemic mixture is an optically inactive mixture due to external compensation.

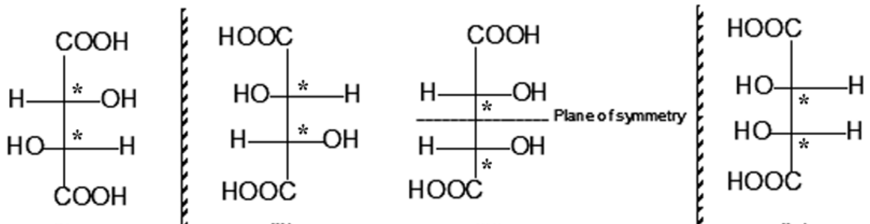
Resolution:

" The process by which a racemic mixture is separated in to its enantiomers (d-form and *l*-form) is called resolution:.

Optical Isomerism of compounds having two asymmetric carbon atoms.

Examples : Tartaric acid or 2, 3 - dihydroxy butane dioic acid.

Since, the compound posses two asymmetric carbon atoms, therefore the no. of isomers formed are $2^n = 2^2 = 4$. They are :



(i) (ii) (iii) (iv)

* marked carbon atoms are asymmetric carbon atom.

Compounds I, II and III, IV are two pair of enantiomers since they are mirror image of each other but not super impossible. But, when compand I is compared with III & IV or compound II is compared with III & IV, it is observed that they are neither mirror image nor superimpossible. They are called diastereo isomers.

Properties of diastereo isomers.

1. They are not mirror image of each other.
2. They are not superimpossible.
3. They have same chemical properties but they may differ in their physical properties.

4. They may rotate the plane of polarised light in the same direction but to different extent.

Out of compound I & II, one of them is d-form and other is in *l*-form . But compound III & IV are optically inactive since they have a plane of symmetry. These two forms are called mesoforms". Mesoform is optically inactive form due to **internal compensation** i.e., if one half of the compound rotate the plane of polarised light in clockwise direction, the other half of the compound rotate the plane of polarised light in anticlockwise direction.

L-104, 105, 106, 107

Introduction to Reaction Mechanism.

1. Inductive Effect (I-effect)

In organic compound, carbon-hydrogen bond in taken to be non-polar i.e., the shared pair of electrons of C–H bond remain exactly midway between them. However any atom or group (say 'X') which is more electro-negative than 'H' is attached to carbon, then the shared pair of electron in C–X bondis more shifted towards 'X' by which carbon develops slight +ve change $(\delta+)$ and 'X' develops slight –ve charge $(\delta-)$.

On the otherhand, if an atom or group (say 'y') which is less electronegative than 'H' is attached to caron, the the shared pair of electrons is more shifted toward carbon than towards 'y' by which carbon develops $\delta-$ and 'Y' develops $\delta+$ charge.

$C:H$ nonpolar

$\overset{\delta+}{C}:\overset{\delta-}{X}$ 'X' is more electronegative than H.

$\overset{\delta-}{C}:\overset{\delta+}{X}$ 'Y' is less electronegative than H

This effect, which is permanent, by which C–X bond or C–Y bond is polarised in known as Inductive effect (I-effect). These are two types.

(i) –I effect : Atoms or groups which are more electronegative than 'H', withdraw electrons towards it are said to possess –I effect (negative Inductive effect).

Example : $-NO_2 > -CN > -COOH > -F > -Cl > -Br$
$> -I > -OH > -OCH_3 > -C_6H_5$ (Phenyl) $> -H$

(ii) **+ I - effect :** Atoms or groups which are less electronegative than 'H' pushes electrons away from it. are said to possess +I effect (positive inductive effect). Examples.

$$(CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2- > CH_3-$$

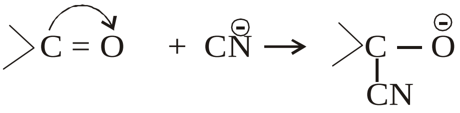
It may be noted that once C–X bond or C – Y bond is polarised, this effect is being felt on the rest of the carbon atoms in the chain.

$$\overset{\delta'''_+}{C}-\overset{\delta''_+}{C}-\overset{\delta'_+}{C}-\overset{\delta_+}{C}\rightarrow\overset{\delta-}{Cl}, \quad \delta^+ > \delta'_+ > \delta''_+ > \delta'''_+$$

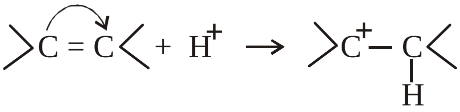
Though, theoretically, all the carbon atoms in the chain develops some amount of charge, but this effect is being felt maximum upto second carbon atom

2. Electromeric Effect (E-effect)

It is a temperary effect. In pressence of charged particle, the shared pair of electrons in a multiple bond moves towards one of the linked atoms is known as electromeric effect. However, when the attacking reagent the charged particle) is removed, the multiple bond regains, its original structure. This effect is of two types.

(i) –E effect 

When the transfer of electrons taken place away from the attacking reagent, it is called –E effect (negative electromeric effect).



(ii) +E effect

When the transfer or electrons take place towards the attacking reagent, it is called +E effect (positive electromeric effect).

Add Figure

3. **Mesomeric effect or Resonance**

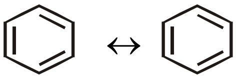
If for a compound or ion, two or more different structures are being written only by differing in the distribution of electron then all these structures are said to be resonating or caloric structures and the phenomenon is known as resonance".

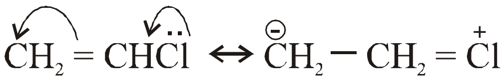
OR

If for a molecular or ion assigned two more structures differing only in the distribution of electron, none of – which is capable of describing all the known properties of the compound, then the actual structure is a resonance hybrid of their structures" The various structures are called resonating or calonical structures and the phenomenon is known as resonance.

Examples

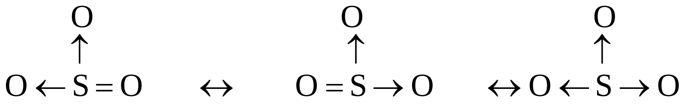
(i) $O \leftarrow S = O \Leftrightarrow O = S \rightarrow O$

(ii) 



$$\ddot{C}H_2 = CH\ddot{C}l \leftrightarrow \overset{\ominus}{C}H_2 - CH_2 = \overset{+}{C}l$$

Stability : More the number of resonating structures, more is the stability of the compound or ion. Thus, SO_3 is more stable than SO_2.



$$\begin{array}{ccccc} O & & O & & O \\ \uparrow & & \uparrow & & \uparrow \\ O \leftarrow S = O & \leftrightarrow & O = S \rightarrow O & \leftrightarrow & O \leftarrow S \rightarrow O \end{array}$$

I II III

Resonance energy : Resonance energy is defined as the difference between the actual energy of the molecule and that of the most stable state of the resonating structures.

+R or +M - effect

Group or atom like –OH, $–NH_2$, X – when conjugated with π-electron system like ethene, butadiene, benzene etc. are capable or releasing some pair or unshared pair of electrons to the system are said to possess +R or + M – effect.

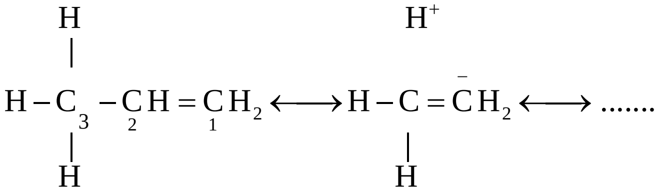
–R or –M – effect

Groups like $–NO_2$,– CHO, –COOH, –CN etc when conjugated with π - electron system like ethene, butadiene, benzene etc. are capable of with drawing electrons from the system are said possess –R or –M effect.

4. Hyper conjugation :

When a C–H bond is attached to an unsaturated system such as double bond benzene ring etc, the sigma (σ) electrons of the C–H bond enters in to conjugation with the unsaturated system. Such conjugation between electrons of single bond (C – H or $\sigma-\text{bond}$) with multiple bond or $\pi-\text{bond}$ is called hyper conjugation".

According to this concept, it an alkyl group carrying at least one hydrogen atom is attached to an unsaturated carbon atom, it released electron of C–H single bond to wards the multiple bond. For example,

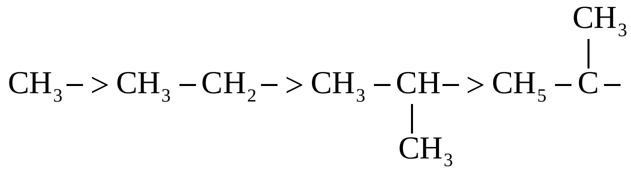


$$\mathrm{H-\underset{H}{\overset{H}{C}}_{3}-\underset{2}{C}H=\underset{1}{C}H_2 \longleftrightarrow H-\underset{H}{\overset{H^+}{C}}=\overset{-}{C}H_2 \longleftrightarrow ....}$$

Thus hyper conjugative structures are different of propene. The existsance of above hyper conjugated structures of propene is evident from the fact that the observed $C_2–C_3$ bond length is 1.49 $\overset{0}{A}$ instead of 1.54 $\overset{0}{A}$ (C–C single bond length).

Since there is no bond between the α - carbon atom and one of its hydrogen atoms, therefore hyperconjugation is sometimes called as no-bond resonance. This concept was developed by Baker and Nathan and sometimes it is called Baker Nathan effect.

→ More the number of $\alpha-H$ atoms conjugated with unsaturated system, more will be then of hyperconjugated structures and hence more is the stability. Thus the order of hyper conjugation is :



$$\mathrm{CH_3- > CH_3-CH_2- > CH_3-\underset{CH_3}{CH}- > CH_5-\overset{CH_3}{C}-}$$

I . $(CH_3)_2 = C(CH_3)_2$, II. $(CH_3)_2C=CH-CH_3$ III. $(CH_3)_2C=CH_2$

IV. $CH_3CH=CH_2$

because cmpound I posses 12 $\alpha-H$ atoms compound II possess 9 $\alpha-H$ atoms, compound III posses 6 $\alpha-H$ atoms and compound IV have only 3 $\alpha-H$

→ Hyper conjugation also explains , why a methyl group is an electron pushing group e.g. Toluene contains 3 $\alpha-H$ and 3-α conjugated structure.

.→ What is the product formed when HBr is treated with pent-2-ene.

Due to hyperconjugation, the π-electrons of C_2–C_3 π bond moves from C_2 to C_3 by which C_2 develops +ve charge and C_3 develops negative charge. Therefore, the negative part of HBr (Br^-) will attack to C_2 carbon atom and the product formed is 2-bromo pentane.

$$CH_3 - CH_2 - CH = CH - CH_3 \xrightarrow{H^+Br^-} CH_3 - CH_2 - CH_2 - CH - CH_3$$

Pent -2-ene 2-Bromopentane

5. Bond Fission

The bond fission or bond breaking takes place in two ways.

(i) **Homolytic fission :** In homolytic fission, the bond breaking of covalent bond takes place is such a key that each atom retains one electron of the shared pair.

$$A:B \xrightarrow[\text{fission}]{\text{homolytic}} A. + B.$$

Free radicals

Homolytic fission of the covalent bond results in the formation of free Homolytic fission of the covalent bond results in the formation of free radicals.

(ii) Heterolytic fission :

In heterolytic fission of the covalent bond the shared pair of electrons is retained by one of the atoms.

$$-\overset{|}{\underset{|}{C}}:X \longrightarrow -\overset{|}{\underset{|}{C}}+ \; + \bar{X}$$

X is more electronegative than C

carbocation

or $$-\overset{|}{\underset{|}{C}}:Y \longrightarrow -\overset{|}{\underset{|}{C}}- \; + Y^+$$

C is more electronegative than Y

6. Types of attacking Reagents:

(i) **Electrophiles :**

Electrophiles are either positivity charged ions or neutral species having deficient of electrons and attack a place where there is more electron density. Examples:

(a) Positively charged electrophiles :

H^+, H_3O^+, Cl^+, NO_2^+, CH_3^+ etc.

(b) Neutral electrophiles

$AlCl_3$, BF_3, SO_2, SO_3, $FeCl_3$ etc.

(ii) **Nucleophiles :** Nucleophiles are either negatively, charged ions or electrically excess neutral species attack a place where there is less electron densitor. Example :

(a) Negatively charged nucleophiles :

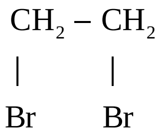
OH^-, CN^-, Cl^-, Br^-, $RCOO^-$ etc.

(b) Neutral Nucleophiles

$$H_2\ddot{O},\ R\ddot{O}H,\ R\ddot{O}R',\ \ddot{N}H_3,\ R\ddot{N}H_2$$

7. Tpes of organism Reactions.

(a) Addition reaction : The reaction in which two molecules react to form a single product is called addition reaction. For example,



$$CH_2=CH_2 \xrightarrow{Br_2} \underset{Br}{CH_2}-\underset{Br}{CH_2}$$ 1,2-dibromo ethane.

(b) substitution reaction : The reaction in which an atom or group is replaced by another atom or group is known as substitution reaction. For example,

$$\underset{\text{methane}}{CH_4+Cl_2} \longrightarrow \underset{\text{Chloromethane}}{CH_3Cl+HCl}$$

(c) Elimination reaction : In this reaction, a small molecule is removed. For example,

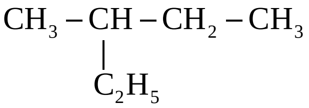
$$\underset{\text{Bormoethene}}{CH_3CH_2Br} \xrightarrow{\text{alc.KOH}} \underset{\text{Ethene.}}{CH_2=CH_2}+KBr+H_2O$$

(d) Rearrangement reaction : This reaction involves the migration of atom or group from are part to another part within the molecule. For example,

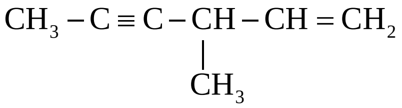
$$\underset{\text{Vinyl alcohol}}{CH_2=CH-OH} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO}$$

HOME ASSIGNMENT

(a) Provide the IUPAC names -

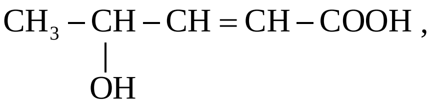


$CH_3-\underset{C_2H_5}{CH}-CH_2-CH_3$,



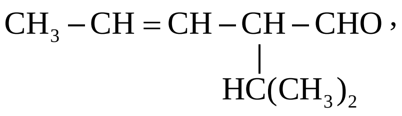
$CH_3-C\equiv C-\underset{CH_3}{CH}-CH=CH_2$

$CH_3-CH=CH-C\equiv C-CH_2OH$, $HO-CH_2-CH=CH-CH_2OH$



$CH_3-\underset{OH}{CH}-CH=CH-COOH$, $(CH_3)_2CH-CH=CH-CH(CH_3)_2$

$CH_3-CH=CH-CH_2-C\equiv N$,



$CH_3-CH=CH-\underset{HC(CH_3)_2}{CH}-CHO$,

$CH_3-CO-CH_2-CH=CH-CHO$, $CH_3-CO-CH_2-CO-CH=CH_2+$

(b) Write the possible of the following and name these isomers.

(i) C_5H_{12} (ii) C_5H_{10} (iii) C_6H_{10}

(iv) $C_4H_{10}O$ (v) C_4H_8O (vi) $C_4H_8O_2$

L-108

METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

Organic compounds whether extracted from a natural source o prepared in the laboratory are never found free from impurities. Various methods used for the purification of organic compound depend on

(i) The nature of the organic compound and

(ii) The nature of the impurity present in it.

The common techniques applied for purification are :

A. CRYSTALLISATION :

(a) Choice of the solvent :

(b) Making the solution :

(c) Hot alteration

(d) Cooling and separation of crystals

(e) Drying

B. SUBLIMATION :

$$\text{Solid} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \text{Vapour}$$

This process is very useful in separating volatile from non-volatile solid but is of limits application as only a few substances like naphthalene, camphor and benzoic acid can be ourified bv this process.

C. DISTILLATION :

The operation of distillation is employed for (i) the separation of volatile liquids from non-volatile impurties and (ii) the liquids having sufficient difference in their boiling points.

Various methods employed for the purification of liquids depend on the nature of the liquid and the nature of impurities present. These are :

(a) Simple distillation :

(b) Fraction distillation :

(c) Distillation under reduced pressure :

This method is applicable to purify liquids having very high boiling points and those, which decompose before their boiling point is reached.

(d) Steam distillation :

Liquid practically immiscible with water, volatile in steam and possessing a fairly high vapour pressure are purified by steam distillation. Steam is bubbled through the impune liquid in a flask heated on a sand bath (Fig.16.13). On vigorous boiling the vapours of the organic substance mixed with steam rise up and condense as they pass through the water condenser. Thus the condensate is a mixture of the organic substance and water. The two, being immiscible are separated in a separating funnel.

D. EXTRACTION WITH A SOLVENT :

The process of removing a substance from its aqueous solution by shaking with a suitable organic solvent is termed extraction.

E. CHROMATOGRAPHY :

Chromatography is an important modem techniques for the separation, isolation, purification and identification of the components present in a mixture. The name derived from Greek words Chroma meaning colour and Graphe meaning writing, suggests that this technique was originally confined to the separation of the coloured substances like plant pigments or dyestuffs, But now this technique is equally applied to colourless substances.

(a) Principle :

Chromatography is based on the principle of selective distribution of the components of a mixture between two phases, a stationary phase and a moving phase. The stationary phase can be a solid or liquid, while the moving phase is a liquid or a gas. When the stationary phase is solid, the basis is **adsorption**, and when it is a liquid, the basis is **partition.**

(b) Types of Chromatography :

Basing on the principle involved, Chromatography can be classified into two different types. These are :

1. Adsorption Chromatography :
   - (i) Column chromatography :
   - (ii) Thin Layer Chromatography (TLC)

$$RF \frac{\text{Distance moved from the base line by the substance}}{\text{Distance moved from the base line by the solvent front}}$$

2. Partition chromatography :

It operates by a mechanism analogous to counter-current distribution. The fixed phase may be a liquid strongly adsorbed on solid which acts as a support. In this case the solute gets distributed between the fixed liquid and the moving liquid (solvent).

Paper chromatography is a special type of partition chromatography in which the water trapped in the cellulose molecules of the paper acts as the stationary phase.

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS :

On heating the mixture, carbon and hydrogen present in the organic compound get oxidized to CO_2 and H_2O respectively.

$$C + 2CuO \xrightarrow{\Delta} 2\,Cu + CO_2$$

$$2H + CuO \xrightarrow{\Delta} Cu + H_2O$$

(i) Water formed converts anhydrous $CuSO_4$ (white) to $CuSO_4$. $5H_2O$ (blue) indicating the presence of hydrogen in the organic compound.

$$CuSO_4 + 5H_2O \rightarrow CuSO_4 .\ 5H_2O$$

Anhydrous copper sulphate (white) Copper sulphate pentahydrate (blue)

(ii) CO_2 formed turns lime water milky indicating the presence of carbon in the organic compound.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$$

lime water

(iii) **Lassaigne's test :** This is a confirmatory test for the detection of nitrogen in all cases of nitrogenous compounds. It involves the following steps.

(a) A freshly cut small piece of sodium metal is melted in a small fusion tube and fused with the organic compound. The red hot tube is broken by immersing in distilled water in a china dish. The contents are boiled in water to extract the fused mass and filtered. This extract is known as sodium fusion extract. Nitrogen if present, combines with sodium and carbon of the organic compound to form sodium cyanide.

$$Na + \underbrace{C + N} \rightarrow NaCN$$

From organic compound

(b) The sodium fusion extract component is boiled with rerrous sulphate solution and cooled.

$FeSO_4 + 2NaOH \rightarrow Fe\ (OH)_2 + Na_2SO_4$

from excess of sodium

$6NaCN + Fe(OH)_2 \quad \rightarrow \quad Na_2\ [Fe\ (CN)J + 2NaOH$

Sodium ferrocyanide.

(c) To the cooled solution a little ferric chloride solution is added followed by excess of conc.hydrochloric acid.

$2Na_4\ [Fe(CN)_6 + 4FeCl_3 \rightarrow Fe_4[Fe(CN)_6]_3 + 12\ NaCl$

Prussian Blue

The formation of Prussian blue or green colouration confirms the presence of nitrogen.

In case sulphur is present along with nitrogen in the organic compound, a blood red colouration may appear while performing the test for nitrogen.

$Na + C + N + S \rightarrow NaCNS$

Sodium sulphocyanide.

$3NaCNS + FeCl_2 \rightarrow Fe\ (CNS)_3 + NaCl$

Ferric Sulphocyanide

(Blood red)

D. Detection of Halogens :

(i) Lassaigne's test: If halogens present in the organic compound, the sodium fusion extract contains sodium halides.

$Na + X \rightarrow NaX$

A little amount of sodium extract is acidified with dilute nitric acid and silver nitrate solution is added to it. A precipitate proves the presence of halogen.

$NaX + AgNO_3 \rightarrow Ag\ x \downarrow + NaNO_3$

White precipitate soluble in dil. NH^OH indicates chlorine. Yellowish white precipitate insoluble in dil. NH_4OH, but soluble in cone. NH_4OH indicates bromine. Yellow precipitate insoluble even in cone. NH_4OH indicates iodine.

(ii) Beilstein test : The copper wire flattened at one end is heated in an oxidizing Bunsen flame till it ceases to impart any green colour to the flame. Now a small amount of organic compound is taken on the copper wire and heated in the flame.

A green flame, if imparted to the flame, is due to the formation of a volatile copper halide and proves the presence of a halogen. Though sensitive, this test is not always reliable for example, urea imparts green colour though it does not contain halogen.

E. Detection of Sulphur :

Sulphur may be detected in an organic compound by the following tests :

(i) **Lassaigne's test:** If sulphur present then the sodium fusion extract contain Na_2S.

$$2Na + S \rightarrow Na_2S$$

Presence of sodium sulphide in the extract can be confirmed as follows :

(a) A purple colour is obtained when a portion of the extract is treated with sodium nitroprusside solution.

$$Na_2S + Na_2\,[Fe(CN)_5NO] \rightarrow \underset{\text{Purple}}{Na_4\,[Fe(CN)_5\,NOS]}$$

(b) A black precipitate of lead sulphide is produced when lead acetate solution is added to the sodium fusion extract.

$$Na_2 + \underset{\text{Lead acetate}}{(CH_3COO)_2Pb} \rightarrow \underset{\substack{\text{Nead suphide}\\ \text{Black ppt}}}{PbS} + 2CH_3COONa$$

QUANTITATIVE ANALYSIS :

A. Estimation of Carbon and Hydrogen (Liebig Method) :

(a) **Principle :** Both carbon and hydrogen are estimated together in one operation. When a known weight of the organic substance is burnt in excess of oxygen, carbon and hydrogen present in it are oxidised to carbon dioxide and water respectively.

$$CxHy + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

The weights of CO and HO thus formed are determined and the amounts of carbon and hydrogen in the original substance calculated.

B. Estimation of Nitrogen : The two main method for the estimation of nitrogen in an organic compound are :

(i) Dumas Method :

(a) **Principles :** Duma's method is based on the fact that nitrogenous compounds when heated with copper oxide in an atmosphere of carbon dioxide yield free nitrogen.

$$C + 2CuO \rightarrow CO_2 + 2Cu$$

$$2H + CuO \rightarrow H_2O + Cu$$

$$2N + CuO \rightarrow N_2 + \text{Oxides of nitrogen}$$

or $C_xH_yN_z + (2x + y/2)\,CuO \rightarrow xCO_2 + y/2\,H_2O + z/2\,N_2 + (2x + y/2)\,Cu$

Traces of oxides of nitrogen formmed, if any are reduced to nitrogen by passing the gaseous mixture over a heated copper spiral.

$$Cu + \text{Oxides of nitrogen} \rightarrow CuO + N$$

The mixture of gases so produced is collected over an aqueous solution of potassium hydroxide which absorbs carbon dioxide. Nitrogen is collected in the uppar part of the graduated tube.

Example : 0.2 gm of an organic compound yielded 20.7 ml of nitrogen at 15°C and 758 mm of Hg by Duma's method. Calculate the percentage of nitrogen in the compound. (Aqueous tension at 15°C = 12mm)

(ii) Kjeldahl's Method :

(a) **Principle :** Kjeldahl's method is based on the fact that when an organic compound containing nitrogen is heated with concentrated sulphuric acid, the nitrogen present in it is quantitavely converted into ammonium sulphate.

$$\underbrace{C+H+N}_{\text{from organic compound}} + \underset{\text{(Conc)}}{H_2SO_4} \xrightarrow{\Delta} CO_2 + H_2O + (NH_4)SO_4$$

The resultant liquid is heated with concentrated alkali and the liberated ammonia gas is passed through a known excess of a standard acid solution. The volume of the unreacted acid is determined by titration with a standard alkali solution. The amount of ammonia and of nitrogen is determined by knowing the amount of acid reacted with ammonia.

$$(NH_4)_2\ SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O\ +\ 2NH_3 \uparrow$$

(d) **Limitation :** This method is not applicable to organic compound containing nitro and azo groups and also to pyridine where nitrogen atom is present in the ring.

Problem : 0.4g of an organic compound on Kjeldahl's analysis gave enough ammonia to just neutralise 20 ml of 0.1 M H_2SO,. Calculate the percentage of nitrogen in the compound.

C. Estimation of Halogens by Carius method :

(a) Principle : Carius method for estimation of halogens is dependent on the fact that when a known weight of the organic compound, containing halogens is heated in the presence of silver nitrate in a hard glass tube known as Carius tube (Fig. 16.23) in a furnace, silver halide is formed. It is filtered, washed, dried and weighed. From the amount of silver halide produced, the percentage of halogen is calculated.

$$\overbrace{C+H+X} + \text{fuming } HNO_3 + AgNO_3 \xrightarrow{\Delta} CO_2 + H_2O + AgX$$

Problem : 0.1890 g of an organic compound gave 0.2870g of silver chloride in Carius method of estimation of halogen. Find out the percentage of chlorine in the compound.

D. Estimation of Sulphur :

(a) **Principle :** A known weight of the organic compound is heated with sodium peroxide or fuming nitric acid in the Carius tube at 300°C for six hours. Sulphur present is oxidised to sulphuric acid which is precipitated as barium sulphate by the addition of excess of barium chloride. Barium sulphate so precipitated is filtered, washed, dried and weighed. The percentage of sulphur can be calculated from the weight of barium sulphate.

$$\underset{\text{(from organic compound)}}{S} + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

$$H_2SO_4 + BaCl_2 \rightarrow \underset{\text{(white ppt.)}}{BaSO_4 \downarrow} + 2HCl$$

Problem : 0.395 g of an organic compound by Carius method for the estimation of sulphur gave 0.582g ofBaSO. Find the precentage of sulphur in the substance.

Solution : Weight of the organic compound = 0.395g

Weight of $BaSO_4$ formed = 0.582g

233g of $BaSO_4$ contains 32g of sulphur

$\therefore$ 0.582g of $BaSO_4$ contains $\frac{32}{233} \times 0.582\text{g}$ of sulphur

Hence, percentage of sulphur in the organic compound

$$= \frac{32}{233} \times 0.582 \times \frac{100}{0.395} = 20.24$$

E. Estimation of Phosphorus :

(a) **Principle :** A known weight of an organic compound is heated with fuming nitric acid in a Carius tube where upon phosphorus present in the compound is oxidised to phosphoric acid (H_3PO_4). The phosphoric acid is precipitated either as (i) ammonium phosphomolybdate, $(NH_4)_3\ PO_4.12\ MoO_3$ by the addition of ammonia and ammonium molybdate solution or (ii) as magnesium ammonium phosphate by adding magnesia mixture ($MgCl_2 + NH_4Cl + NH_4OH$) which on ignition yeilds magnesium pyrophosphate. .

$$\underset{\text{Magnesium ammonium phosphate}}{2MgNH_4PO_4} \rightarrow \underset{\text{Magnesium pyrophosphate}}{Mg_2P_2O_7} + 2NH_3 + H_2O$$

Precipitate of ammonium phosphomolybdate or /magnesium pyrophosphate is separated, dried and weighed from which the percentage of phosphorus can be calculated.

F. Estimation of Oxygen :

Though the percentage of oxygen in an organic compound is obtained by substracting the sum of the percentages of other elements from 100, it can be estimated by a direct method.

(a) **Principle :** A known weight of the organic compound is pyrolysed in a stream of nitrogen gas. The mixture of gaseous products along with oxygen is passed over red hot coke (1373K) when all the oxygen is converted to carbon monoxide. This when passed through warm (448K) iodine pentoxide (10) is oxidised to carbon dioxide producing iodine (Fig. 16.24)

$$\text{Organic compound} \xrightarrow{\Delta} O_3 + \text{Gaseous products}$$

$$2C + o_2(g) \xrightarrow{1373K} 2CO(g)$$

$$5CO + I_2O_5 \xrightarrow{448K} 5CO_2 + I_2$$

By determining the amount of CO- (or I) produced, the percentage of oxygen in the original organic compound can be calculated, which can be done by passing the mixture of CO and I- over a bed of potassium iodide solution, thus removing iodine. The residual gases containing CO^ are finally passed through a soda-asbestos U-tube where CO^ is retained. This U-tube is weighed before and after pyrolysis, the difference of which gives the amount of CO^ obtained from the given sample of the organic compound.

G CHN Analyser :

Recently it has become possible to carry out the estimation ‘of elements like carbon, hydrogen and nitorgen present in an organic compound by using only micro quantities (1-3 mg) of the compound and automatic experimental techniques like CHN Analyser. This instrument displays the results on a screen within a short time.

L-109, 110, 111, 112, 113, 114.

ALKANE

Prepare of alkanes

G.F. C_nH_{2n+1}, $n = 1, 2, ...\infty$ or RH

It does not possess any specific functional group, but carbon carbon single bond may be treated as functional group.

‘In alkanes each carbon atom undergoes sp^3 hybridisation

Alkane usually exhibit chain isomerism,

General methods of preparation

(A) From alkylhalide

Statement :

[**Zn-Cu couple :** Zn metal is wrapped by Cu-metal.

Zn react with ethyl alcohol (ethanol) produces hydrogen which act as reducing agent. Cu act as catalyst.

Alkyl halide - (G. F) - RX]

$$RX \xrightarrow[\text{Zn}-\text{Cu}]{[H]} RH + HX$$

Couple

$+ C_2H_5OH$

e.g.

$$CH_3Cl \xrightarrow[\text{Zn}-\text{Cu}]{[\,H\,]} CH_4 + HCl$$

Couple

$+ C_2H_5OH$

$$CH_3CH_2Br \xrightarrow[\text{Zn}-\text{Cu Couple}]{[\,H\,]} CH_3CH_3 + HBr$$

$+ C_2H_5OH$

Statement :

$$R\boxed{X + 2Na + X}\;R \xrightarrow[\text{ether}]{\text{Dry}} 2NaX + R - R\ (\text{Alkane})$$

e.g. $CH_3\boxed{Cl + 2Na + Cl}CH_3 \xrightarrow[\text{ether}]{\text{Dry}} 2NaCl + CH_3 - CH_3$ (ethene)

e.g. $CH_3CH_2\boxed{Br + 2Na + Br}CH_2CH_3 \xrightarrow[\text{ether}]{\text{Dry}}$

$2NaBr + CH_3CH_2CH_2CH_3$ (Butane)

e.g. CH_3 and CH_3CH_2Cl

(i) $CH_3Cl + 2Na + ClCH_3 \xrightarrow[\text{ether}]{\text{Dry}} 2NaCl + CH_2{-}CH_3$ (Ethane)

(ii) $CH_3CH_2Cl + 2Na + ClCH_2CH_3 \xrightarrow[\text{ether}]{\text{Dry}} 2NaCl + CH_3CH_2{-}CH_2CH_3$ (Butane)

(iii) $CH_3Cl + 2Na + ClCH_2CH_3 \xrightarrow[\text{ether}]{\text{Dry}} 2NaCl + CH_3CH_2CH_3$ (Propane) (ethane & butane as impurities)

- CH_4 can not be prepared by this process.

(B) From mono carboxylic acid.

(1) Decarboxylation :

Statement :

- Sodalime is a mixture of NaOH (Soda) and CaO (lime)

$$RCOONa \xrightarrow[+CaO]{NaOH} RH + Na_2CO_3 + CaO$$

$$\Delta \ 630\,K$$

Sodium alkanoate

e.g. $$CH_3COONa \xrightarrow[+CaO]{NaOH} CH_4 + Na_2CO_3 + CaO$$

$$\Delta$$

Sod. ethanoate

$$CH_3CH_2COONa \xrightarrow[+CaO]{NaOH} CH_3CH_3 + Na_2CO_3 + CaO$$

$$\Delta$$

Sod. propanoate

(The presence of CaO smoothens the reaction)

(2) Kolbe's Electrolysis : (Kolbe's Electrolysis is a general method for the preparation of alkane, alkene, alkyne.)

$$\begin{array}{lclcl} 2RCOOK & & 2RCOO^- & + & 2K^+ \\ \text{Potassium} & \xrightleftharpoons{\text{Electrolysis}} & \text{Alkanoate} & & \text{Potassium} \\ \text{alkanoate} & & \text{ion} & & \text{ion} \end{array}$$

At cathode : $2K^+ + 2e^- \rightarrow 2K$

$2H_2O + 2e^- \rightarrow 2OH^- + H_2\uparrow$

At anode : $$\begin{array}{l} RCOO^- \\ RCOO^- \end{array} \xrightarrow[\text{(ii) } -2CO_2]{\text{(i) } -2e^-} \begin{array}{c} R-R \\ \text{Alkane} \end{array}\uparrow$$

[CO_2 is arested by NaOH or KOH]

$$\begin{pmatrix} 2KOH + CO_2 \rightarrow K_2CO_3 + H_2O \\ 2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \end{pmatrix}$$

$$2CH_3COOK \xrightleftharpoons{\text{Electrolysis}} 2CH_3COO^- + 2K^+$$

Potasium ethanoate.

At cathode : $2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^-$

At anode :

$$\begin{matrix} CH_3COO^- \\ CH_3COO^- \end{matrix} \xrightarrow[(ii)\ -2CO_2]{(i)\ -2e^-} \begin{matrix} CH_3 - CH_3 \uparrow \\ \text{Ethane} \end{matrix}$$

(C) From unsaturated hydrocarbons (Hydrogenation of alkene / alkyne) :

Statement :

$$\underset{\text{Alkene}}{RCH = CH_2} \xrightarrow[Ni\ (200-300^0 C)]{H_2(g)} \underset{\text{Alkane}}{RCH_2 - CH_3}$$

or

Pt / Pd at $25^0 C$

e.g. $$\underset{\text{Alkene}}{CH_2 = CH_2} \xrightarrow[Ni(200-300^0 C)]{H_2(g)} CH_3 - CH_3 \text{ (Ethane)}$$

or

Pt / Pd at $25^0 C$

$$\underset{\text{Alkyne}}{RC \equiv CH} \xrightarrow[Ni(200-300^0 C)]{H_2(g)} \underset{\text{Alkene}}{RCH = CH_2} \rightarrow \underset{\text{Alkane}}{RCH_2 - CH_3}$$

or

Pt / Pd at $25^0 C$

e.g. $$\underset{\text{Ethyne}}{CH \equiv CH} \xrightarrow[Ni(200-300^0 C)]{H_2(g)} \underset{\text{Ethene}}{CH_2 = CH_2} \xrightarrow[Ni(200-300^0 C)]{H_2(g)} \underset{\text{Ethane}}{CH_3 - CH_3}$$

or

Pt / Pd at $25^0 C$ $\quad$ Pt / Pd at $25^0 C$

(Methane can not be prepared by this process since methane contain 1 carbon atom where as alkene or alkyne contain minimum 2 carbon atoms)

(D) **From Grignard's Reagent** : (Alkyl magnesium halide is known as Grignard's reagent.)

Statement :

(Active hydrogen atom : Hydrogen atom becomes, active when it is attached to oxygen, nitrogen, sulpher etc.)

$H - O \boxed{H + R} MgX \rightarrow RH + Mg\ (OH) \times$ (Magnesium hydroxy halide)

e.g. $H - O - \boxed{H + CH_3} MgBr \rightarrow CH_4 + Mg\ (OH)\ Br$

(Magnesium hydroxy bromide)

$R' - O - \boxed{H + R} MgX \rightarrow RH + Mg\ (OR') \times$ (Magnesium alkoxy halide)

e.g. $CH_3CH_2 - O - \boxed{H + CH_3} MgBr \rightarrow Mg\ (OC_2H_5)Br$

(Magnesium Ethoxy bromide)

E. **Corey - House Synthesis**

During this process alkyl groups, two different alkyl halide are coupled by lithium and cuprous iodide to form an unsymmetrical alkane.

In this method, one alkyl halide is converted to alkyl lithium (RLi) which react with CuI to form lithium dialkyl cupric (R_2CuLi). It is then treated with other alkyl halide $(R'X)$ to get an unsymmetrical alkane $(R-R')$

Example :

$$CH_3I + 2Li \longrightarrow CH_3Li + LiI$$

$$2CH_3Li + CuI \longrightarrow (CH_3)_2\,CuLi + LiI$$

$$(CH_3)_2\,CuLi + C_2H_5I \longrightarrow \underset{\text{Propane}}{CH_3 - CH_2CH_3} + CH_3Cu + LiI$$

Similarly, pentane can be prepared by using CH_3CH_2Br and $CH_3CH_2CH_2Br$.

Chemical properties :

(A) **Substitution reaction :** substitution reaction of alkanes are 3 types.

(i) Halogenation

(ii) Nitration

(iii) Sulphonation

(i) **Halogenation :** The halogenetion reaction of alkanes are also two types :

(a) F_2, Cl_2 and Br_2 in one way.

(b) The behaviour of I_2 towards alkane is different.

$F_2 > Cl_2 > Br_2$

(c) Reactivity of alkane $3^0 > 2^0 > 1^0 > -CH_3$

The reaction of Cl_2, F_2, Br_2 with alkane are also two types

i) **With diffused sunlight :** The presence of diffused sunlight, the halogenation is a multi step process i.e. halogenation continues till all the hydrogen atoms are substituted by halogen.

e.g. $CH_4 + Cl_2 \xrightarrow[\text{Sun-light}]{\text{Diffused}} CH_3Cl + \xrightarrow[-HCl]{Cl_2} CH_2Cl_2$

$\xrightarrow{Cl_2} CHCl_3 + HCl \xrightarrow{Cl_2} HCl + CCl_4$ (Carbon tetrachlorine)

* Carbon tetra chloride is used as foam-type fire extinguisher.

* Organic compound having no. 'H' atom - CCl_4, CS_2.

This reaction of halogens with alkane in presence of diffused sunlight proceed through free radical mechanism or free radical substitution.

Initiation. $Cl:Cl \xrightarrow[\text{Sun-light}]{\text{In diffused}} Cl. + Cl.$

Propagation $CH_4 + .Cl \rightarrow .CH_3 + HCl$

$.CH_3 + Cl - Cl \longrightarrow CH_3Cl + .Cl$

Termination: $Cl. + .Cl \longrightarrow Cl - Cl$

$CH_3. + .Cl \longrightarrow CH_3Cl$

(During this reaction, sometimes ethane also produced due to:

$$CH_3.+CH_3. \rightarrow (CH_3-CH_3)$$

ii) **In presence of direct sunlight; In**

$$CH_4+2Cl_2 \xrightarrow[\text{Sun-light}]{\text{Direct}} C+4HCl$$

iii) **With Iodine :** The reaction of Iodine with alkane is very very slow and reversible in nature.

$$CH_4+I_2 \rightleftharpoons CH_3I+HI,$$

Reaction proceeds in forward direction in preence of HNO_3 / HIO_3 (oxidant).

Q. Why direct lodination of alkane are not being carried out ?

Reasons : The reaction is very very slow. The reaction is also reversible in nature)

Nitration :

Statement :

$$R\boxed{H+HO}NO_2 \rightarrow RNO_2+H_2O \text{ (Nitroalkane)}$$

Theoritically all alkanes can be nitrated but practically hexane and higher members are easy to nitrate due to their existance in same phase.

$$C_6H_{13}\boxed{H + HO}NO_2 \rightarrow H_2O + C_6H_{13}\ NO_2 \text{ (Nitrohexane)}$$

Hexane

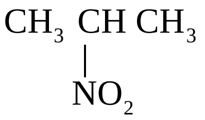
Recently vapour phase nitration is being carried out with lower alkanes between 400 to 440°C.

$$CH_4 + HNO_3 \text{ (vapour)} \xrightarrow{400\text{-}440°C} CH_3NO_2 + H_2O$$

$$CH_3CH_3 + HNO_3 \text{ (vapour)} \xrightarrow{400\text{-}440°C} CH_3CH_2NO_2 + H_2O$$

$$CH_3CH_2CH_3+HNO_3 \text{ (vapour)} \xrightarrow{400\text{-}440°C}$$

i) $CH_3CH_2CH_2NO_2$ (1-nitropropane)+H_2O

ii) 

$$\underset{\displaystyle NO_2}{CH_3\ \underset{|}{CH}\ CH_3}$$ 2-nitropropane +H_2O

iii) CH_3NO_2 nitromethane + H_2O

iv) $CH_3CH_2NO_2$ nitroethane + H_2O

(iii) Sulphonation :

Statement :

$$R\boxed{H + HO}SO_3H \rightarrow H_2O + RSO_3H \text{ (alkane sulphonic acid)}$$

Theoritically all alkanes can be sulphonated but practically hexane and higher members are easy to sulphonated due to their existence in same phase (liquid).

e.g. $C_6H_{13}H + HOSO_3 \rightarrow H_2O + C_6H_{13}SO_3H$ (hexane sulphonic acid)

(B) Oxidation

(i) Combustion : (When substance burns in the presence of O_2, the process is called combustion).

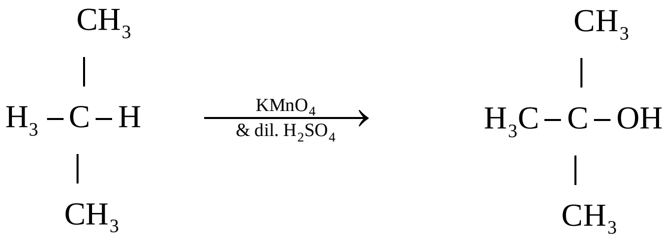
e.g. $CH_4 + 2O_2 \xrightarrow{\Delta} CO_2 + 2H_2O + \text{Heat}\uparrow$ (Energy)

(ii) Catalytic oxidation :

$$2CH_4 + O_2 \xrightarrow[400^0\,C \;\&\; 200\,atm]{Cu} 2CH_3OH$$

iii) Chemical oxidation : (When oxidation is carried out by using oxidising agent known as chemical oxidation).

- Alkanes are not usually oxidised by using chemical oxidising agents.
- However alkanes having tertiary carbon atom can be oxidised to corresponding alcohol when oxidised by using acidified potassium permanganate ($KMnO_4$).
- (Tertiary carbon atom : When one carbon atom-attached to three more carbon atom, it is called tertiary carbon atom.) (Acidified $KMnO_4$: $KMnO_4$ mixed with dil.H_2SO_4)



$$H_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-H \xrightarrow[\&\ dil.\ H_2SO_4]{KMnO_4} H_3C-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH$$

(2-methyl propane (iso-butane) (2-methyl propanol-2-ol)

C) Cracking

When pyrolysis is applied to hydrocarbons, the process is called craking.

- **Pyrolysis :** (Breaking a compound by the affect of heat is known as pyrolysis.)

When a higher saturated hydrocarbon is heated in presence of catalyst at high temperature and high pressure but in absence of air or oxygen breaks to form lower hydrocarbon is known as cracking.

$$C_8H_{18} \xrightarrow[\text{High Pressure \& high temperature}]{\text{Catalyst}} C_4H_8 + C_4H_{10},\ C_5H_{10} + C_3H_8$$

$$C_2H_6 + CH_4 + C + H_2,\ C_5H_{12} + C_3H_6$$

D) Aromatisation : (The process by which an aliphatic compound is converted to an aromatic compound known as aromatisation).

Statement :

$$\text{hexane} \xrightarrow[600^0\,C\ \&\ 15\ atm]{Al_2O_3 + Cr_2O_3} \text{Benzene}$$

$$CH_3(CH_2)_5{-}CH_3 \xrightarrow[600^0\,C\ \&\ 15\ atm]{Al_2O_3 + Cr_2O_3} \text{Toluene}$$

ALKENES :

G. F. – $C_n H_{2n}$, n =2, 3 ....

F. G. – Carbon carbon double bond (C=C)

- Carbon atom having double bond will undergo sp^2 hybridisation.
- Alkene usually exhibit position isomerism and also geometrical isomerism.

Preparation ;

$CH_2 = CH_2$

Ethene (Ethylene)

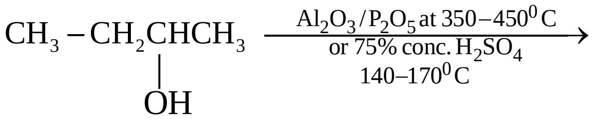
1) **Dehydration of alcohol ;** When alcohol is treated with dehydroting agents like Al_2O_3/ P_2O_5 at 350–450°C or by using 75% cone. H_2SO_4 between 140-170"C gives alkene.

- **Dehydrating agent:** The chemicals which takes water formed during a chemica! reaction is known as dehydrating agent.
- **Drying agent:** The chemicals which take free water molecules is called drying agent.

$$RCH_2 - CH_2 - OH \xrightarrow[\substack{\text{or } 75\% \text{ conc. } H_2SO_4 \\ 140\text{–}170^0 C}]{Al_2O_3/P_2O_5 \text{ at } 350-450^0 C} RCH = CH_2$$

$$CH_3 - CH_2OH \xrightarrow[\substack{\text{or } 75\% \text{ conc. } H_2SO_4 \\ 140\text{–}170^0 C}]{Al_2O_3/P_2O_5 \text{ at } 350-450^0 C} CH_2 = CH_2$$

Ethanol Ethylene



$$\underset{\substack{| \\ OH}}{CH_3 - CH_2CHCH_3} \xrightarrow[\substack{\text{or } 75\% \text{ conc. } H_2SO_4 \\ 140\text{–}170^0 C}]{Al_2O_3/P_2O_5 \text{ at } 350-450^0 C}$$

i) $CH_3CH_2CH=CH_2$ and ii) $CH_3CH=CH–CH_3$

(but-1-ene, 20%) (but-2-ene, 80%) (major)

(minor) (decided by saytze's rule)

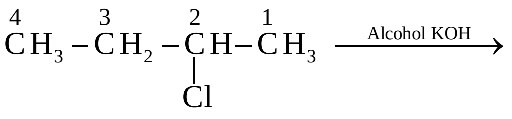
2) **Dehydrohalogenation of alkyl halide :** When alkyl halide is treated with alcoholic potassium hydroxide gives alkene.

- **(Alcoholic KOH :** When KOH dissolues in ethyl alcohol, it is called alcoholic KOH.)

$$RCH_2\,CH_2X \xrightarrow{\text{Alcoholic KOH}} RCH = CH_2 + KX + H_2O$$

$$CH_3\,CH_2Cl \xrightarrow{\text{Alcoholic KOH}} CH_2 = CH_2 + KCl + H_2O$$

(Chloroethane) (Ethylene)



$$\overset{4}{C}H_3 - \overset{3}{C}H_2 - \underset{\substack{| \\ Cl}}{\overset{2}{C}}H - \overset{1}{C}H_3 \xrightarrow{\text{Alcohol KOH}}$$

2-chloro Butane

i) $CH_3CH_2CH = CH_2 + KCl + H_2O$ ii) $CH_3CH = CH–CH_3 + KCl + H_2O$

(But-1-ene, 20%) (But-2-ene, 80%)

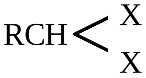
(decided by Saytzev's rule)

- Saytzev's rule : When a secondary alcohol or tertiary alcohol is dehydrated or when a secondary alkyi halide or tertiary alkyi halide is dehydrohalogenated, an alkene is formed which is more alkyl substituted.

3) Dehalogenation of vic-dihalide

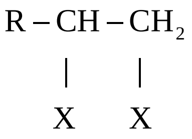
❖ Dihalides are of two types

i) When two halogen atoms attached to same ‘C’-atom, it is called Gem-dihalide



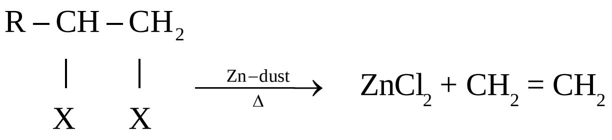
$$RCH<\begin{matrix}X\\X\end{matrix}$$

ii) When two halogen-atoms are attachted to two adjacent ‘C’ atoms, it is called vicdihalide.



$$\begin{array}{ccccc}R-&CH&-&CH_2\\&|&&|\\&X&&X\end{array}$$

When vic dihalide is heated with zinc dust, it gives alkene.

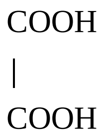


$$\begin{array}{ccccc}R-&CH&-&CH_2\\&|&&|\\&X&&X\end{array}\xrightarrow[\Delta]{Zn-dust}ZnCl_2+CH_2=CH_2$$

(1, 2-dichloro ethane)

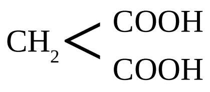
4) Kolbe’s Electrolysis :

(Examples of dicarboxylic acid



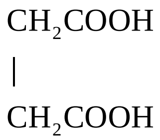
$$\begin{array}{l}COOH\\|\\COOH\end{array}$$

(Oxalic acid. Ethane dioic acid)



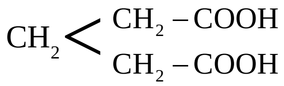
$$CH_2<\begin{matrix}COOH\\COOH\end{matrix}$$

(Malonic acid, propanedioic acid)



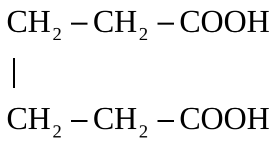
$$\begin{array}{l}CH_2COOH\\|\\CH_2COOH\end{array}$$

(Succinic acid, Butanedioic acid)



$$CH_2<\begin{matrix}CH_2-COOH\\CH_2-COOH\end{matrix}$$

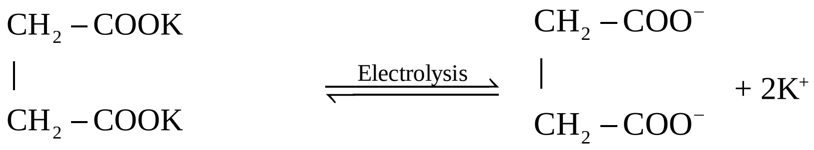
(Glutaric acid, Pentanediocic acid)



$$\begin{array}{l}CH_2-CH_2-COOH\\|\\CH_2-CH_2-COOH\end{array}$$

(Adipic acid, hexanedioic acid)

When saturated aqueous solution of sodium or potassium salt of dicarboxylic acid on electrolysis gives alkene. (at anode)

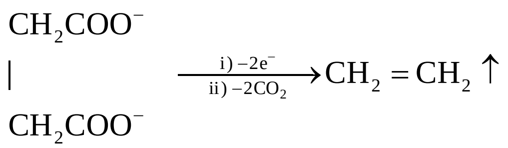


$$\begin{array}{l}CH_2-COOK\\|\\CH_2-COOK\end{array}\xrightleftharpoons{Electrolysis}\begin{array}{l}CH_2-COO^-\\|\\CH_2-COO^-\end{array}+2K^+$$

Potassium Succinate　　Succination　　Potassium ion

At cathode **At anode**

$$2H_2O + 2e^- \rightarrow 2O\overline{H} + H_2 \uparrow$$



$$\begin{array}{l} CH_2COO^- \\ | \\ CH_2COO^- \end{array} \xrightarrow[\text{ii) } -2CO_2]{\text{i) } -2e^-} CH_2 = CH_2 \uparrow$$

$$(2KOH + CO_2 \rightarrow K_2CO_3 + H_2O)$$

5) By partial hydrogenation of alkynes :

Statement :

Lindlar's catalyst : Pd is partially deactivated by using heavy metal salt or quinoline is known as Lindlar's catalyst.

$$RC \equiv CH + H_2 \xrightarrow[(200-300^0 C)]{Ni} RCH = CH_2$$

$$1 : 1$$

$$RC \equiv CH + H_2 \xrightarrow[\text{Catalyst}]{\text{Lindlar's}} RCH = CH_2$$

$$CH \equiv CH + H_2 \xrightarrow[(200-300^0 C)]{Ni} CH_2 = CH_2$$

$$1 : 1$$

Acetylene Ethylene

$$CH \equiv CH + H_2 \xrightarrow[\text{Catalyst}]{\text{Lindlar's}} CH_2 = CH_2$$

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Properties :

A) Addition reaction :

i) Addition of hydrogen (hydrogenation) :

$$RCH = CH_2 \xrightarrow[Ni\,(200-300^0 C)]{H_2} RCH_2 - CH_3$$

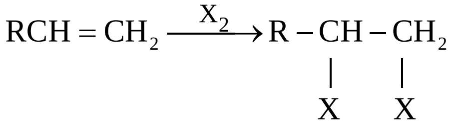
or

$$Pt / Pd \text{ at } 25^0 C$$

$$CH_2 = CH_2 \xrightarrow[Ni\,(200-300^0 C)]{H_2} CH_3 - CH_3$$

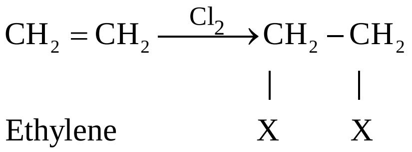
Ethylene Ethane

ii) Addition with halogens :



$$RCH = CH_2 \xrightarrow{X_2} \begin{array}{l} R - CH - CH_2 \\ \quad\;\;\, | \quad\;\;\; | \\ \quad\;\;\, X \quad\;\, X \end{array}$$

Alkene Vic – dihalide

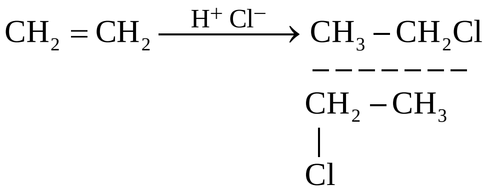


$$CH_2 = CH_2 \xrightarrow{Cl_2} \begin{array}{l} CH_2 - CH_2 \\ \;\; | \qquad\; | \\ \;\; X \qquad X \end{array}$$

(1, 2-dichloroethane)

Ethylene

iii) Addition with hydrogen halide : Markownikoff's rule



$$CH_2 = CH_2 \xrightarrow{H^+ Cl^-} CH_3 - CH_2Cl$$

$$\begin{array}{l} CH_2 - CH_3 \\ | \\ Cl \end{array}$$

Reagent	(Substrate (unsaturated Hydrocarbon)	No. of product
symmetrical H–H X–X	symmetrical / unsymmetrical hydrocarbons	1
unsymmetrical	symmetrical	1
unsymmetrical	unsymmetrical	2

Markownikoff's Rule :

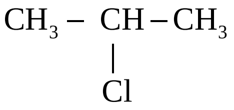
When an unsymmetrical molecule is added to an unsymmetrical, unsaturated hydrocarbon, the addition product formed is governed by Markownikoff's rule.

According to this rule, the negative part of the addendum or additive reagent will attach to carbon atom having least number of hydrogen.

When propene react with HCI two products are formed, they are 1-chloropropane and 2-chloropropane.

$$CH_3 - CH - CH_2 \xrightarrow{H^+ Cl^-}$$

i) $CH_3 - CH_2 - CH_2Cl$ (ii)



$$\begin{array}{l} CH_3 - CH - CH_3 \\ \quad\quad\;\; | \\ \quad\quad\; Cl \end{array}$$

1-chloro propane 2-chloropropane

But according to Markownikoff's rule, 2-chloropropane will be formed but not 1-chloropropane.

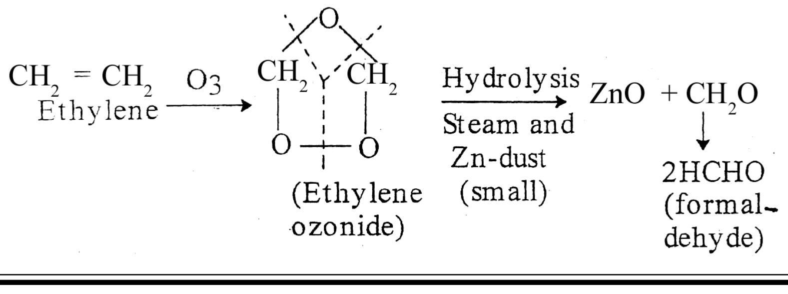
However when HBr is treated yvith an unsymmetrical, unsaturated hydrocarbon in presence of organic peroxide, the negative part (Br) will attach to carbon atom having more no. of hydrogen.

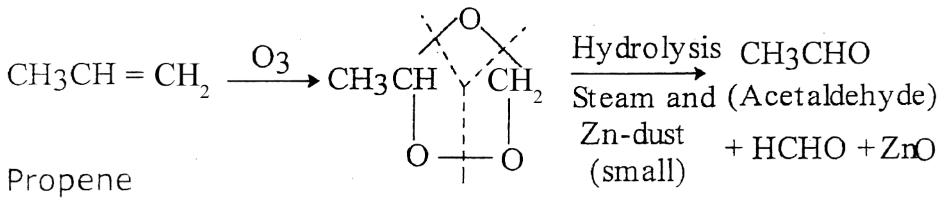
This effect is called peroxide effect or anti Markownikoff's rule.

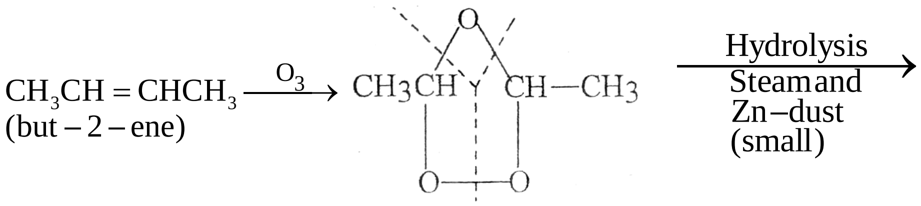
e.g. → $CH_3CH = CH_2 \xrightarrow[\text{Organic peroxide}]{H^+ Br^-} CH_3CH_2 - CH_2Br$ $(1 - \text{bromo Pr opane})$

iv) Ozonolysis : Ozonolysis is a two-step process. Addition of ozone and subsequent hydrolysis of ozonide so formed is called ozonolysis.

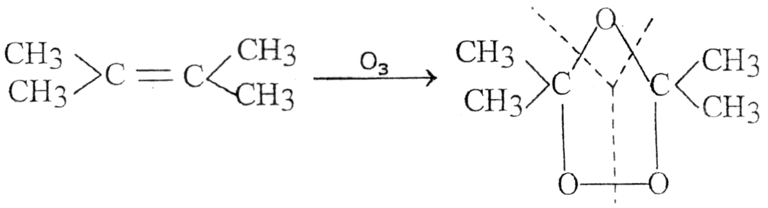
e.g.



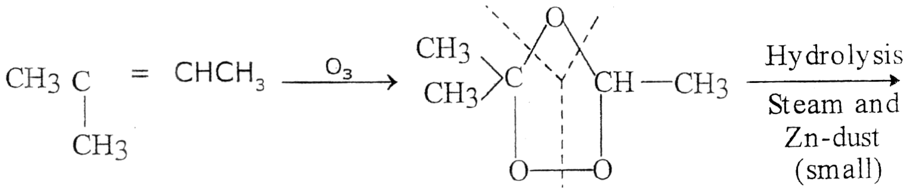




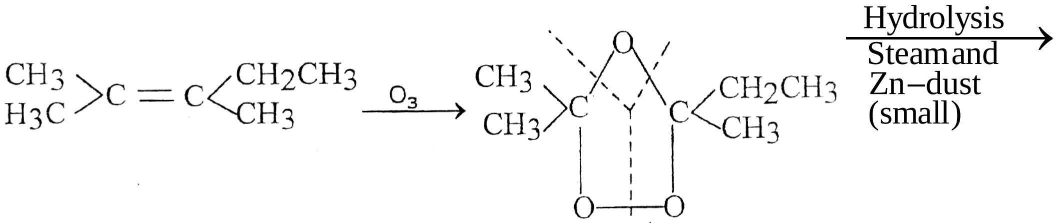
ZnO + 2CH_3CO (Acetone)

e.g. 

(2, 3-dimethyl but-2-ene) ZnO + 2CH_3COCH (Acetone)

e.g. 

(2 methyl but-2-ene) ZnO + CH_3CHO+CH_3COCH_3 (Aldehyde-ketone)
Acetaldehyde

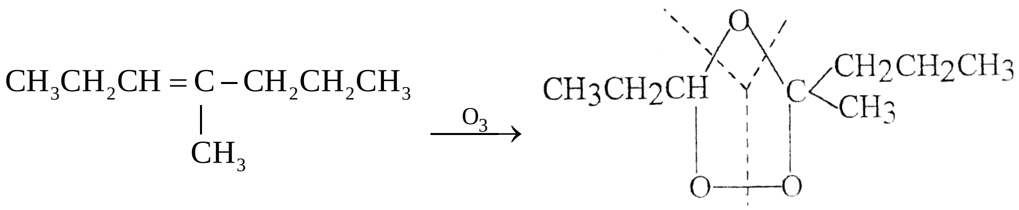
e.g. 

(2, 3-dimethyl pent-2-ene) ZnO+CH_3COCH_3 + $CH_3COCH_2CH_3$
Acetone 2-butanone

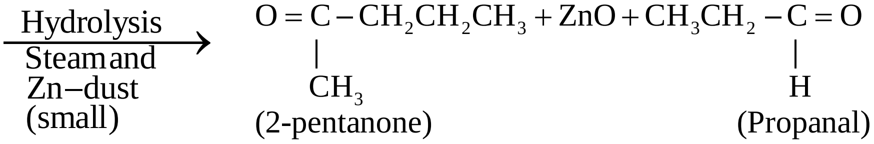
Ozonolysis is a tool or method to decide the position of double bond in alkene.

Helps to descend C-atom in chain.

Ans. suppose on ozonolysis an alkene, we get pentan-2-one and propanal. Then the alkene will be 4-methyl hept-3-ene.

e.g. 

(4-methyl hept - 3- ene)



$$\xrightarrow[\text{Steam and Zn–dust (small)}]{\text{Hydrolysis}} \underset{\text{(2-pentanone)}}{\underset{\displaystyle CH_3}{\underset{|}{O=C}}-CH_2CH_2CH_3} + ZnO + \underset{\text{(Propanal)}}{CH_3CH_2-\underset{\displaystyle H}{\underset{|}{C}}=O}$$

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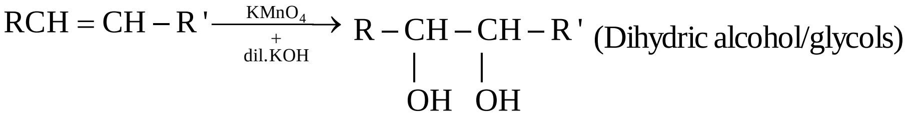
B) Oxidation

i) Combustion :

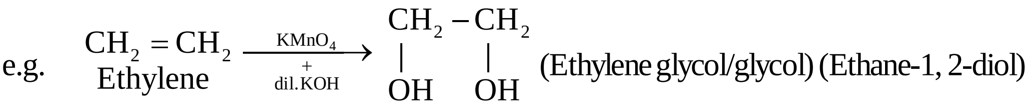
e.g. $CH_2=CH_2+O_2 \xrightarrow{\Delta} CO_2+H_2O+\text{Heat}\uparrow$

ii) **Using alkaline $KMnO_4$:** ($KMnO_4$ mixed with dil. KOH or NaOH)

Statement :



$$RCH=CH-R' \xrightarrow[\text{dil.KOH}]{KMnO_4 \, +} R-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-R' \text{ (Dihydric alcohol/glycols)}$$



e.g. $$\underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow[\text{dil.KOH}]{KMnO_4 \, +} \underset{\displaystyle OH}{\underset{|}{CH_2}}-\underset{\displaystyle OH}{\underset{|}{CH_2}} \text{ (Ethylene glycol/glycol) (Ethane-1, 2-diol)}$$

iii) **Oxidation by using acidified $KMnO_4$:**

Statement :

$$RCH=CH-R' \xrightarrow[\text{dil.}H_2SO_4]{KMnO_4 \, +} RCOOH+R'COOH$$

e.g. $$\underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow[\text{dil.}H_2SO_4]{KMnO_4 \, +} \underset{\text{(formic acid)}}{2\,HCOOH} \xrightarrow{[O]} CO_2+H_2O$$

C) Polymerisation : When a same molecule (monomer) is repeated for large no. of time inpresencce of catalyst at high temperature and under high pressure is known as polymerisation. When alkene is polymerised, gives polyalkene.

$$\underset{\text{Ethene}}{nCH_2=CH_2} \xrightarrow[\text{High Temp. \& Catalyst}]{\text{High pressure}} \underset{\text{Polythene}}{-(CH_2-CH_2)_n-}$$

D) Isomerisation :

Statement :

$$\underset{\text{Pent-1-ene}}{CH_3CH_2CH_2CH=CH_2} \xrightarrow[200–300^0C \; \Delta]{Al_2(SO_4)_3} \underset{\text{Pent}-2-\text{ene}}{CH_3CH_2CH=CH-CH_3}$$

E) Substitution : Alkene usually does not undergo substitution reaction. However when propene treated with chlorine at high temperature (500°C) gives allylchloride after substitution.

e.g. He= CH–CH_3 $\xrightarrow[500^0C]{Cl_2}$ $\underset{\text{Allychloride}}{CH_2=CH-CH_2Cl}$ + HCl

$$\begin{bmatrix} \text{Allyl} & CH_2=CH-CH_2- \\ \text{Vinyl} & CH_2=CH_2- \end{bmatrix}$$

Uses :

- Gaseous alkenes like kerosene oil or petrol are used as fuel in laboratory and industry.
- Since they burn with a black sooty flame/ they are used for making lamp black which is further used in black inks and paints.
- Ethylenes are used in synthesis of other organic compounds.
- Poly Vinyl Chloride (PVC) which are plastic like solids are largely used in industry for making wire insulation, toys/ foot wear and many such like things.

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ALKYNES :

G.F. – $C_n H_{2n-2}$, n = 2, 3,............ ∞

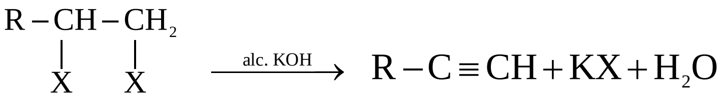
F.G. = Carbon carbon triple covalent bond

First member : HC ≡ CH (Acetylene/Ethyne). 'C' atoms having triple bond undergoes sp-hybridisation.

lkynes exhibit position isomerism.

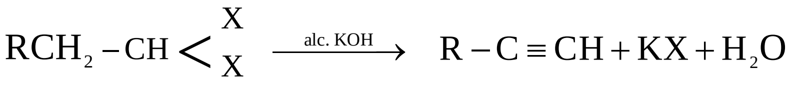
A) General methods of preparation ;

i) Dehydrohalogenation of dihalides :



$$\underset{X}{R-CH}-\underset{X}{CH_2} \xrightarrow{\text{alc. KOH}} R-C\equiv CH+KX+H_2O$$

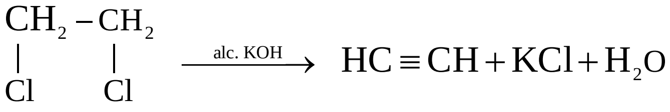
Vic – Dihalide



$$RCH_2-CH{<}^{X}_{X} \xrightarrow{\text{alc. KOH}} R-C\equiv CH+KX+H_2O$$

Gem.-dihalide

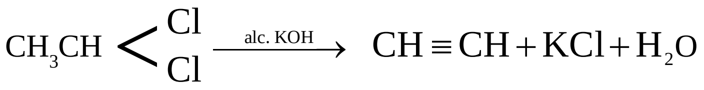
e.g.



$$\underset{Cl}{CH_2}-\underset{Cl}{CH_2} \xrightarrow{\text{alc. KOH}} HC\equiv CH+KCl+H_2O$$

1,2-dichloro ethane Acetylene

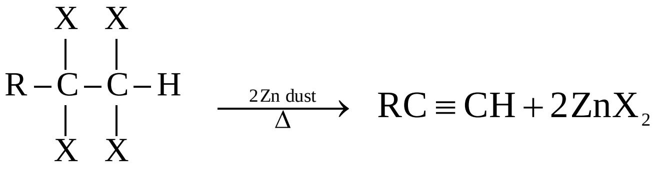
e.g.



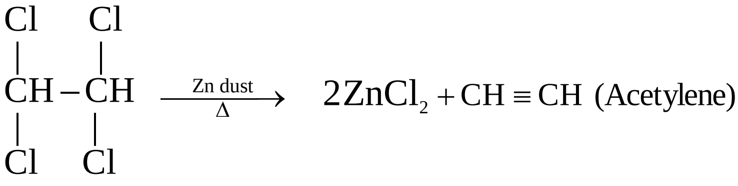
$$CH_3CH{<}^{Cl}_{Cl} \xrightarrow{\text{alc. KOH}} CH\equiv CH+KCl+H_2O$$

(1,1-dichloro ethane) Acetylene

2) Dehalogenation of symmetrical tetrahalide.



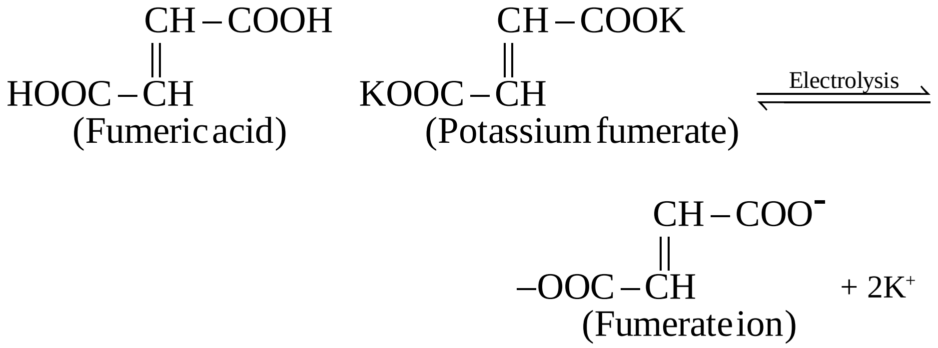
$$R-\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}-H \xrightarrow[\Delta]{\text{2Zn dust}} RC\equiv CH+2ZnX_2$$



$$\overset{Cl}{\underset{Cl}{CH}}-\overset{Cl}{\underset{Cl}{CH}} \xrightarrow[\Delta]{\text{Zn dust}} 2ZnCl_2+CH\equiv CH \text{ (Acetylene)}$$

(1, 1, 2, 2-tetra chloroethane)

3) Kolbe's electrolysis : Saturated aqueous solution of Na or K salt of unsaturated dicarboxylic acid on electrolysis gives alkyne.

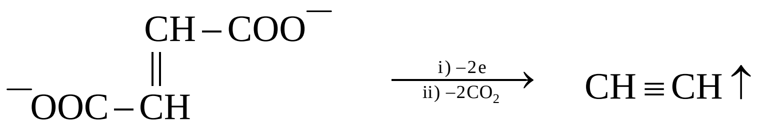


$$\underset{\text{(Fumeric acid)}}{\begin{array}{c}\text{CH}-\text{COOH}\\ \|\\ \text{HOOC}-\text{CH}\end{array}} \quad \underset{\text{(Potassium fumerate)}}{\begin{array}{c}\text{CH}-\text{COOK}\\ \|\\ \text{KOOC}-\text{CH}\end{array}} \xrightleftharpoons{\text{Electrolysis}} \underset{\text{(Fumerate ion)}}{\begin{array}{c}\text{CH}-\text{COO}^-\\ \|\\ -\text{OOC}-\text{CH}\end{array}} + 2K^+$$

At Cathode

$$2H_2O + 2e^- \longrightarrow H_2\uparrow + 2OH^-$$

At Anode



$$\begin{array}{c}\text{CH}-\text{COO}^-\\ \|\\ ^-\text{OOC}-\text{CH}\end{array} \xrightarrow[\text{ii) }-2CO_2]{\text{i) }-2e} \underset{\text{Acetylene}}{CH\equiv CH\uparrow}$$

$(2KOH+CO_2 \longrightarrow K_2CO_3+H_2O)$

4) Hydrolysis of metallic alkynides : When metallic alkynides are treated with water give alkynes.

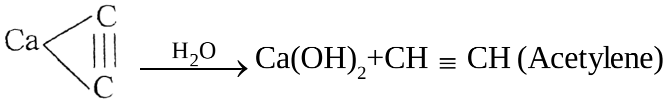
$$R-C\equiv CM \xrightarrow{H_2O} RC\equiv CH + MOH,$$

$M \rightarrow$ Monovalent metal

((Metallic alkynides)

Preparation of only acetylene

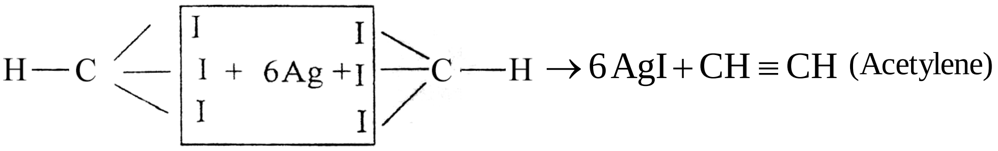
1) When CaC_2 (Calcium carbide) is treated with H_2O gives acetylene.



$Ca(OH)_2 + CH\equiv CH$ (Acetylene)

(Calcium carbide)

2) When Iodo-form is treated with metallic silver gives acetylene.



$\rightarrow 6AgI + CH\equiv CH$ (Acetylene)

Chemical Properties

A) Addition reactions

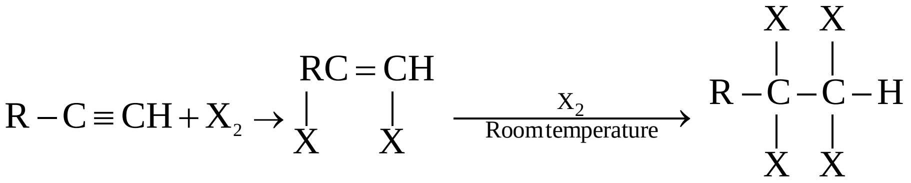
1) Addition with hydrogen (hydrogeneration) :

Statement :

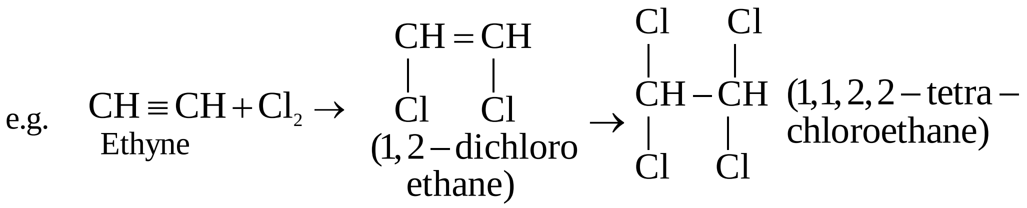
$$\underset{\text{Alkyne}}{R-C\equiv CH + H_2(g)} \xrightarrow[\substack{200\text{–}300^0C\\ \text{and}\\ Pt/Pd\text{ at }25^0C}]{Ni} \underset{\text{Alkene}}{RCH=CH_2} \rightarrow \underset{\text{Alkane}}{RCH_2-CH_3}$$

$$\underset{\text{Acetylene}}{CH\equiv CH + H_2(g)} \xrightarrow[\substack{200\text{–}300^0C\\ \text{and}\\ Pt/Pd\text{ at }25^0C}]{Ni} \underset{\text{Ethylene}}{CH_2=CH_2} \rightarrow \underset{\text{Ethane}}{CH_3-CH_3}$$

2) Addition with halogen (halogenation) :

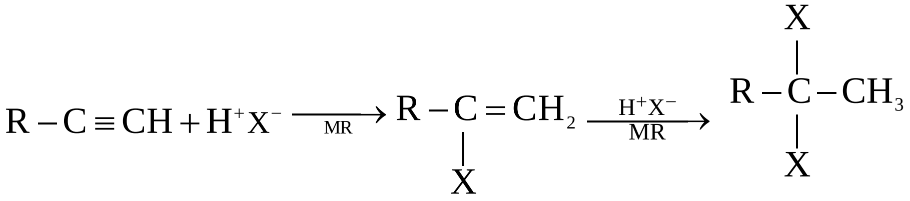


$$R-C\equiv CH+X_2 \rightarrow \underset{X}{RC}=\underset{X}{CH} \xrightarrow[\text{Room temperature}]{X_2} R-\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}-H$$



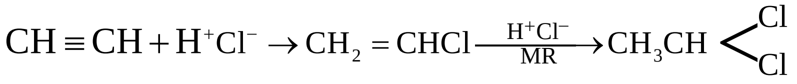
e.g. $$\underset{\text{Ethyne}}{CH\equiv CH+Cl_2} \rightarrow \underset{\text{(1, 2 – dichloro ethane)}}{\underset{Cl}{CH}=\underset{Cl}{CH}} \rightarrow \overset{Cl}{\underset{Cl}{CH}}-\overset{Cl}{\underset{Cl}{CH}} \text{ (1,1,2,2 – tetra – chloroethane)}$$

3) Addition with hydrogen halide :



$$R-C\equiv CH+H^+X^- \xrightarrow[MR]{} R-\underset{X}{C}=CH_2 \xrightarrow[MR]{H^+X^-} R-\overset{X}{\underset{X}{C}}-CH_3$$

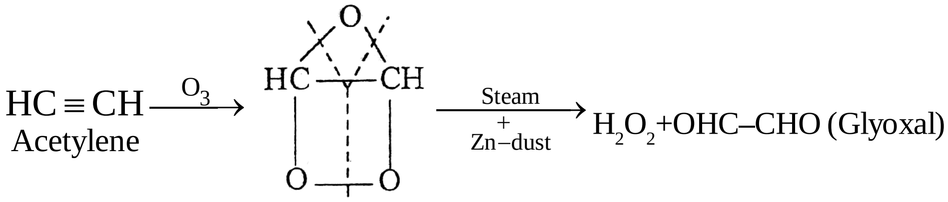
(Gem-dihalise)
MR = Markownikoff's rule.



$$CH\equiv CH+H^+Cl^- \rightarrow CH_2=CHCl \xrightarrow[MR]{H^+Cl^-} CH_3CH\begin{matrix}Cl\\Cl\end{matrix}$$

(Gem-dihalide (1, 1-dichloro ethane)

4) Addition with ozone / Ozonolysis : When alkyne is ozonolised gives a dicarboxylic acid.



$$\underset{\text{Acetylene}}{HC\equiv CH} \xrightarrow{O_3} \xrightarrow[\text{Zn–dust}]{\text{Steam} \; +} H_2O_2+OHC–CHO \text{ (Glyoxal)}$$

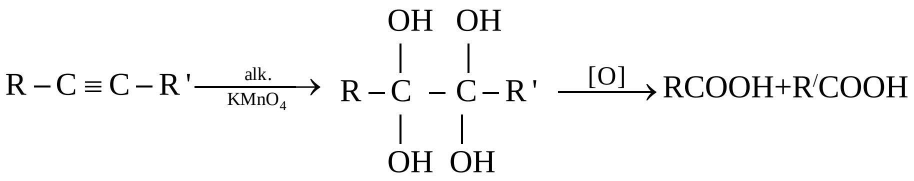
$$\underset{\text{Glyoxal}}{OCH-CHO} \xrightarrow[H_2O_2]{[O]} \underset{\text{(oxalic acid)}}{HOOC-COOH} \xrightarrow{\Delta} HCOOH+CO_2$$

B) Oxidation reactions

Statement :

i) $HC\equiv CH+O_2 \xrightarrow{\Delta} CO_2+H_2O+\text{Heat}\uparrow$

ii) Oxidation by using alk. $KMnO_4$: When alkyne is oxidised in presence of alk. $KMnO_4$ gives two mono-carboxylic acids.



$$R-C\equiv C-R' \xrightarrow[KMnO_4]{\text{alk.}} R-\overset{OH}{\underset{OH}{C}}-\overset{OH}{\underset{OH}{C}}-R' \xrightarrow{[O]} RCOOH+R'COOH$$

(More than one hydroxide group attach the same ‘C’ atom, makes the compound unstable)

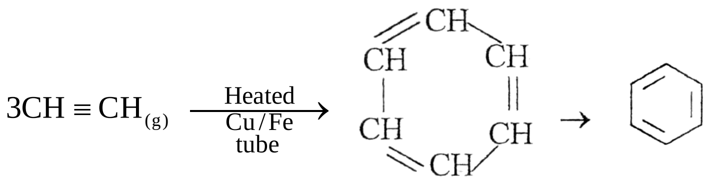
e.g. $$HC \equiv CH \xrightarrow[KMnO_4]{alk.} OHC-CHO \xrightarrow{[O]} 2HCOOH$$

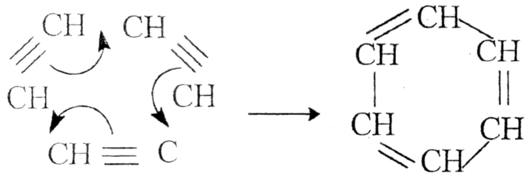
$$RC \equiv CH \xrightarrow[Dil.H_2SO_4]{K_2Cr_2O_7} RCH_2-COOH$$

$$CH \equiv CH \xrightarrow[Dil.H_2SO_4]{K_2Cr_2O_7} CH_3-COOH$$

Acetylene Acetic acid

C) **Polymerisation :** When acetylene is passed through heated copper or iron tube, 3 molecules of it polymerises to form benzene.





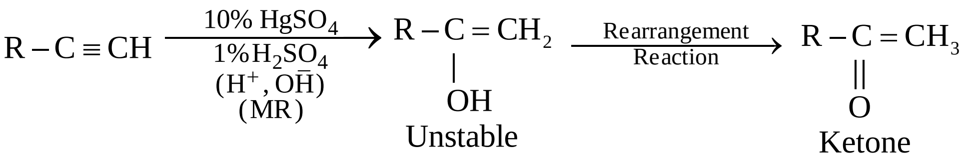
Benzene

Action with acidified mercuric sulphate :

(a) When acetylene is treated with 10% $HgSO_4$ mixed with 1% H_2SO_4 give acetaldehyde.

$$\underset{\text{Acetylene}}{CH \equiv CH} \xrightarrow[\substack{1\%H_2SO_4 \\ (H^+, \bar{O}H)}]{10\% \; HgSO_4} \underset{\substack{\text{Vinylalcohol} \\ \text{(unstable)}}}{CH_2 = CHOH} \xrightarrow[\text{Reaction}]{\text{Rearrangement}} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

(b) When any alkyne other than acetylene is treated with acidified mercuric sulphate, forms ketone.



$$R-C \equiv CH \xrightarrow[\substack{1\%H_2SO_4 \\ (H^+, \bar{O}H) \\ (MR)}]{10\% \; HgSO_4} \underset{\text{Unstable}}{R-\underset{OH}{\underset{|}{C}}=CH_2} \xrightarrow[\text{Reaction}]{\text{Rearrangement}} \underset{\text{Ketone}}{R-\underset{O}{\underset{||}{C}}=CH_3}$$

Uses : Oxy-acetylene flame is used for welding.

2) Acetylene is used for ripening of fruits.

L-114

I) Distinction between saturated hydrocarbons and unsaturated hydro carbons:

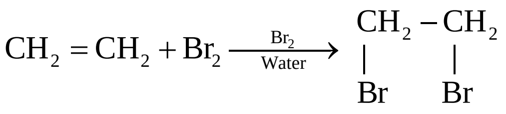
(Bromine water : When bromine mixed with water, it is called bromine water. It’s colour is yellow brown).

When ethane is passed through bromine water there is no change in the colour of bromine water since ethane does not react with it.

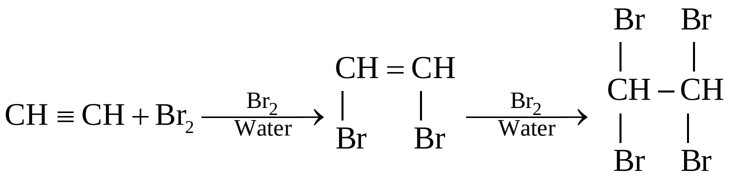
$$\underset{\text{Ethane}}{CH_3-CH_3} \xrightarrow[\text{Water}]{Br_2} \text{No reaction}$$

(Hence no change in the colour of Br;, water)

When ethylene or acetylene is passed through bromine water, the yellowish brown colour of bromine water becomes colourless or the colour of bromine water is discharged since both ethylene and acetylene react with bromine water since they are unsaturated hydrocarbons.



$$CH_2=CH_2+Br_2 \xrightarrow[Water]{Br_2} \begin{array}{cc} CH_2 - & CH_2 \\ | & | \\ Br & Br \end{array}$$



$$CH\equiv CH+Br_2 \xrightarrow[Water]{Br_2} \begin{array}{cc} CH = & CH \\ | & | \\ Br & Br \end{array} \xrightarrow[Water]{Br_2} \begin{array}{cc} Br & Br \\ | & | \\ CH - & CH \\ | & | \\ Br & Br \end{array}$$

II) Distinction between ethylene and acetylene

The conventional method like using bromine water can not be used here since both ethylene and acetylene decolourises bromine water as both of them are unsaturated hydrocarbons and undergo addition reaction with Br_2.

Acidic H-atom

Alkynes like acetylene contain acidic hydrogen atom since this hydrogen atom can be replaced by active metals. (When H-atom is replaced by active metals, it is called acidic H-atom).

Q. Why hydrogen atom of acetylene is acidic in nature ?

Ans. In acetylene 'C' undergoes sp hybridisation. Since it contains 50% s-character it is acidic in nature.

Based upon the principle that acetylene contain acidic hydrogen atom, the following methods are used to distinguish between ethyeene and acetylene.

1) **Action with metallic sodium or sodamide ($NaNH_2$) :** When acetylene gas is passed through heated sodium or sodamide/ forms monosodium acetylide and disodium acetylide.

$$CH\equiv CH \xrightarrow[\substack{NaNH_2 \\ \Delta}]{Na} \begin{array}{l} CH\equiv CNa \leftarrow \text{Monosodium acetylide} \\ \quad \text{and} \\ NaC\equiv CNa \leftarrow \text{Disodium acetylide} \end{array}$$

Both mono-sodium acetylide and disodium acetylide are colourless products. (Ethylene does not under go any reaction with Na or $NaNH_2$)

2) **Action with ammonical cuprous chloride :** (Ammoniacal cuprous chloride- Cu_2Cl_2 + NH_4OH)

When acetylene is passed through ammoniacal cuprous chloride, it forms a reddish brown ppt. of copper acetylide.

$$CH\equiv CH \xrightarrow[NH_4OH]{Cu_2\,Cl_2} CCu\equiv CCu\downarrow + NH_4Cl + H_2O$$

(Copper acetylide)
Reddish brown ppt.

3) **Action with ammoniacal silver nitrate :** ($AgNO_3$ mixed with NH_4OH forms ammoniacal silver nitrate).

When acetylene is passed through ammoniacal silver nitrate solution forms a white ppt. of silver acetylide.

$$CH \equiv CH \xrightarrow[NH_4OH]{AgNO_3} AgC \equiv CAg \downarrow + NH_4NO_3 + H_2O$$

(silver acetylide)
white ppt.

- Ethylene does not undergo any of the above reaction.
- Reactions 2 and 3 are distingwishing tests since they form coloured ppt. But, reaction 1 gives colourless products.

Q_6 - Which of the following compounds responds above three tests ?

i) $CH_3 - C \equiv C - CH_3$, But – 2 – yne

ii) $CH_3CH_2C \equiv CH$ But –1– yne

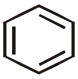
Therefore, But-1-yne respond above three tests as it contains acidic H.

L-115, 116, 117, 118

1. These compounds possess aroma (smell) and hence called aromatic.
2. They are cyclic in nature (i.e., contain one or more rings).
3. All the elements present are in one plane which facilitate resonance.
4. They are unsaturated compounds but behave like a saturated compounds i.e. instead of undergoing addition reactions, they prefer substitution reactions.
5. They satisfy Huckel's Rule, which states that 'an organic compound becomes aromatic in nature when it contain (4n+2) number of π -electrons', (n=0, 1, 2, 3......). The π -electron is one which does not undergo hybridination.

For example, Benzene is an aromatic compound due to :

i) It has smell (aroma)

ii) It is cyclic in nature 

iii) It is planner in nature since all the carbon atoms undergoes sp^2-hybridination. (Bond angle is 120°, trigonal planner).

iv) It prefer substitution reaction rather than addition reaction.

v) It satisfies Huckel's rule. i.e. it contains 6-π-electrons, as all its six carbon atoms undergo sp^2-hybridisation.

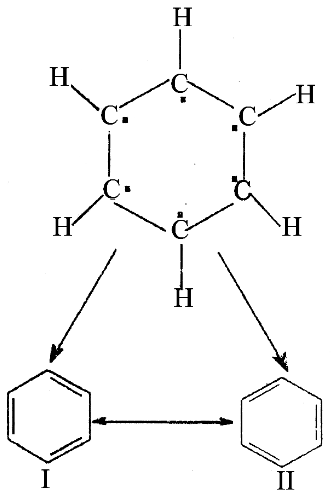
E.C. of carbon in ground state

$$1s^2 \quad \boxed{\uparrow\downarrow} \qquad 2s^2 \quad \boxed{\uparrow\downarrow} \qquad 2p^2 \quad \boxed{\uparrow}\boxed{\uparrow}\boxed{}$$

E.C. of carbon in excited state

$$1s^2 \quad \boxed{\uparrow\downarrow} \qquad 2s^2 \quad \boxed{\uparrow} \qquad 2px^1 \; 2py^1 \; 2pz^1 \quad \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$$

When carbon undergoes sp^2 hybridination one of its p-orbital remain unhybridised known as π-electrons. Therefore 6- carbon atoms possess 6π electrons which satisfy Huckel's rule $(4 \times 1 + 2 = 6\pi \text{ electrons}, n = 1)$.



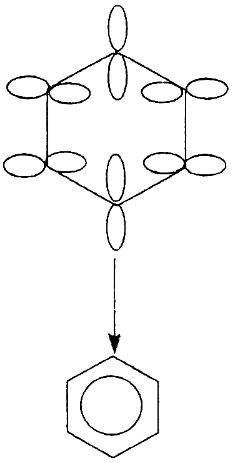
Compound I and II are two resonating structures of benzene.

These 6π-electrons are delocalised in nature and hence double bond is not fixed and therefore benzene prefers substitution reaction rather than addition reaction. If the double bond would have been fixed, there would have been two types of bond length.

i) 3 no. of $C-C \rightarrow 1.54\ \overset{0}{A}$

ii) 3 no. of $C=C \rightarrow 1.33\ \overset{0}{A}$

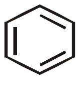
But in benzene all the carbon carbon bond lengths are equal and it is $1.397\ \overset{0}{A}$. Therefore, the 6 n delocalised electrons sandwitches the planner hexagonal benzene ring.

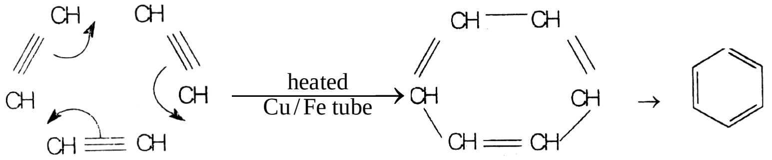


A. Preparation of benzene from Aliphatic compounds :

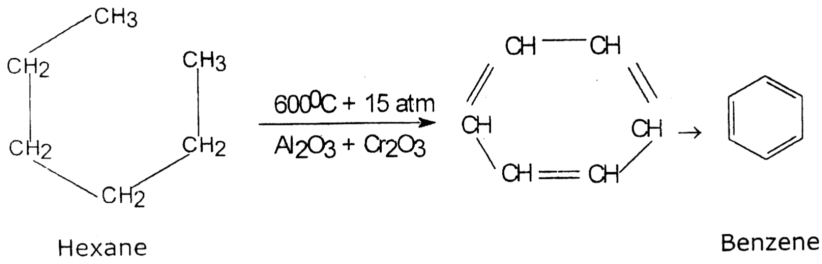
From Acetylene : When acetylene (gas) is passed through heated copper tube or irontube, three molecule of its, combines to form benzene.

$$3CH\equiv CH(g)\xrightarrow[\text{Cu/Fe tube}]{\text{heated}}\underset{\text{Trimer}}{C_6H_{6(\ell)}}\rightarrow$$





2. **From Hexane :** When hexane is heated in presence of Al_2O_3 and Cr_2O_3 mixture at 600°C and 15 atm pressure, aromatises to from benzene.



B. From Aromatic compounds :

1. **From phenol :** When phenol is heated with Zn-dust producess benzene.

$$C_6H_5-OH \xrightarrow[\Delta]{\text{Zn dust}} C_6H_6 + ZnO$$

2. **From benzoic acid :** When benzoic acid or sodium benzoate is heated with sodalime, forms benzene.

$$C_6H_5COONa + NaOH \xrightarrow[\Delta]{\text{CaO}} C_6H_6 + Na_2CO_3$$

3. **From benzenesulphonic acid :** When benzene sulphonic acid hydrolysed by super heated steam, forms benzene :

$$C_6H_5SO_3H \xrightarrow[130^0-150^0C]{\text{Steam}} C_6H_6 + H_2SO_4$$

4. **From benzene diazonium chloride :** When benzene diazonium chloride is reduced with hypophosphorus acid (H_3PO_2) benzene is formed.

$$C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow C_6H_6 + H_3PO_3 + N_2 + HCl$$

Physical properties :

- **i)** Benzene is a colourless liquid.
- ii) It possess aroma.
- iii) Its boiling point is 81°C
- iv) It is carcinogenic in nature.

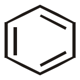
Chemical Properties :

A. Substitution Reaction : Substitution reactions are of three types.

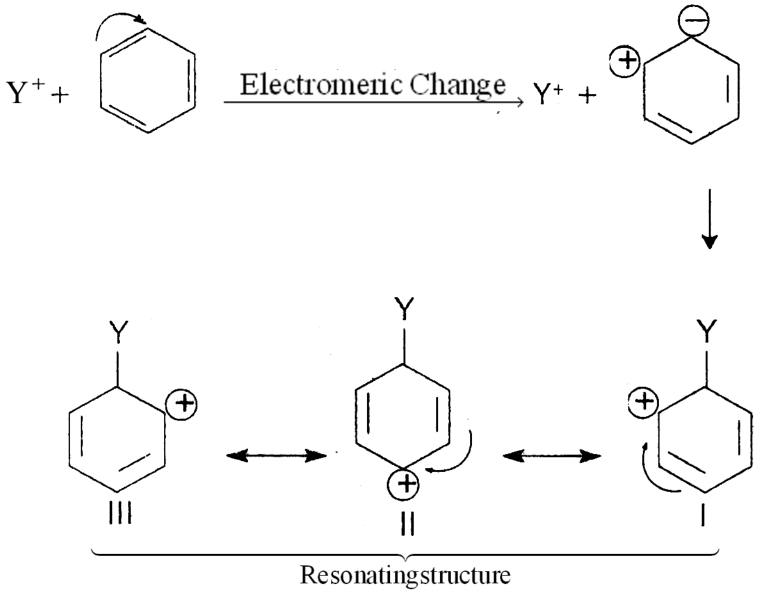
- i) Free radical substitution
- ii) Electrophillic substitution
- iii) Nucleo phillic substitution

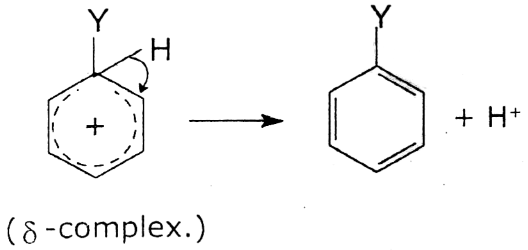
Benzene undergoes electrophillic substitution reaction. The over all mechanism of electrophillic substitution reaction is as follows.

Y^+ → Electrophile → The reagent

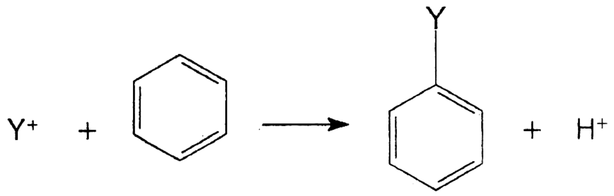
 → substrate → Where the reaction takes place.

In presence of an electrophile, the substrate undergo an electromeric change.



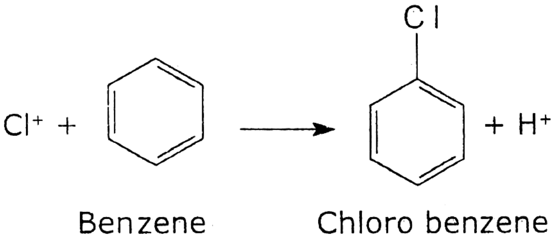


The overall reaction is :



1. **Halogenatron :** Benzene reacts with chlorine or bromine in presence of Lewis acid (Halogen carrier), like $FeCl_3$ or $FeBr_3$ forms chlorobenzen.e or bromo benzene.

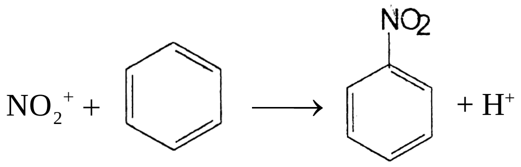
$$Cl_2 + FeCl_3 \rightarrow \underset{\text{Chlorium ion}}{Cl^+} + FeCl_4^-$$



$$H + FeCl_4^- \longrightarrow FeCl_3 + HCl$$

2. Nitration : Nitration of benzene is carried'out in presence of-conc. HNO_3 and cone. H_2SO_4 mixture.

$$HNO_3 + H_2SO_4 \longrightarrow \underset{\text{Nitronium ion}}{NO_2^+} + HSO_4^- + H_2O$$

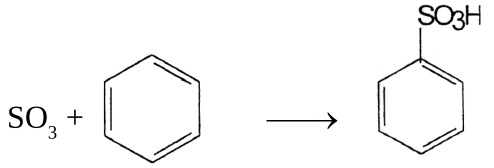


Benzene Nitrobenzene

$$H^+ + HSO_4^- \longrightarrow H_2SO_4$$

3. **Sulphonation :** benzene is sulphonated when treated with conc. H_2SO_4 or fuming H_2SO_4 (H_2SO_4 + SO_3).

$$H_2SO_4 \longrightarrow H_2O + SO_3$$

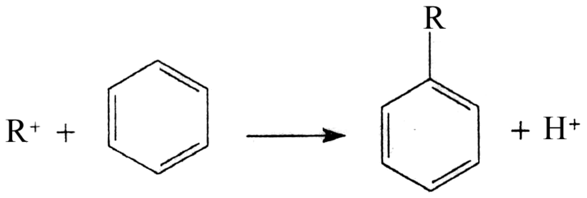


Benzene Benzene Sulphonic Acid

4. **Fridel Craft reaction :**

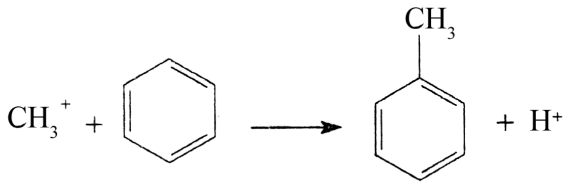
i) **Alkylation :** Benzene is alkylated when treated with alkyl halide in presence of anhy. $AlCl_3$ (Lewis acid)

$$RCl + AlCl_3 \longrightarrow AlCl_4^- + R^+$$



$$H^+ + AlCl_4^- \longrightarrow AlCl_3 + HCl$$

$$CH_3Cl + AlCl_3 \longrightarrow CH_3^+ + AlCl_4^-$$

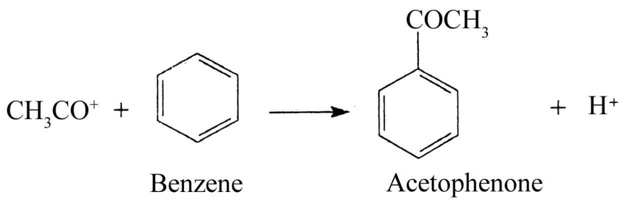


Benzene Toluene

$$H^+ + AlCl_4^- \longrightarrow AlCl_3 + HCl$$

ii) **Acylation :** Benzene is acylated when treated with acetyl chloride in presence of anhydrous $AlCl_3$.

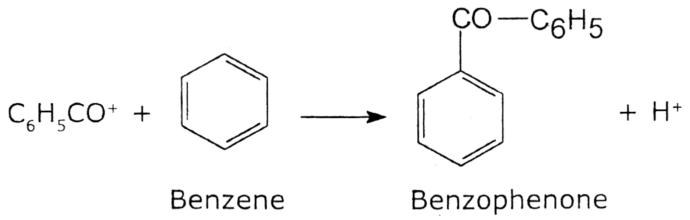
$$CH_3COCl + AlCl_3 \longrightarrow CH_3CO^+ + AlCl_4^-$$



$$H^+ + AlCl_4^- \longrightarrow AlCl_3 + HCl$$

iii) **Benzoylation :** benzene is benozoylated when treated with benzoyl chloride in presence of anhydrous $AlCl_3$.

$$C_6H_5COCl + AlCl_3 \longrightarrow C_6H_5CO^+ + AlCl_4^-$$

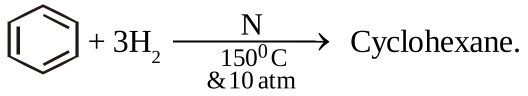


$$H^+ + AlCl_4^- \longrightarrow AlCl_3 + HCl$$

B. Addition reaction :

01. Addition with hydrogen.

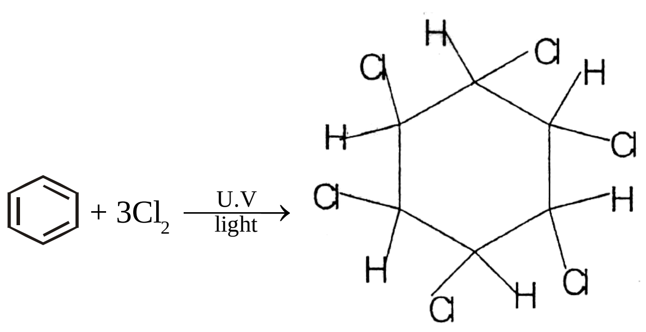
Statement :



(C_6H_6) Benzene

02. **Addition with chlorine :**

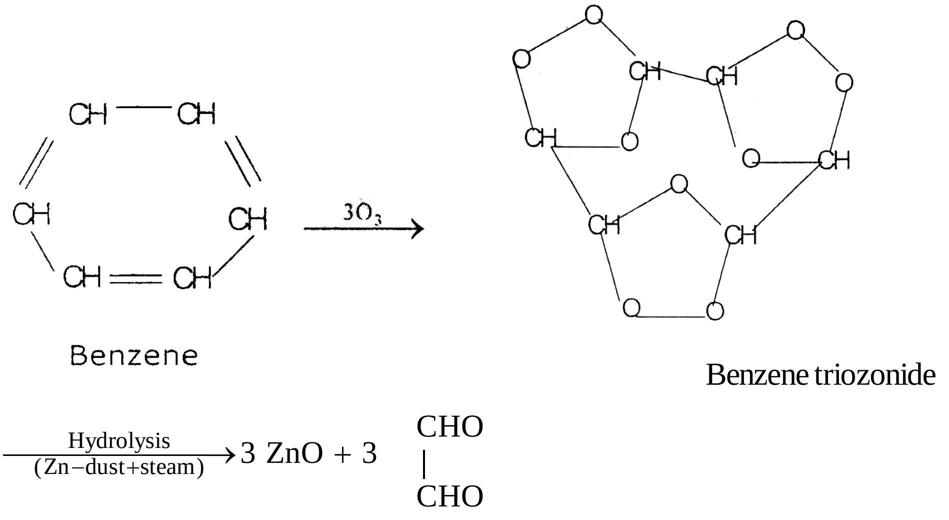
Statement :



(C_6H_6) Benzene BHC or Gamaxene. ($C_6H_6Cl_6$)

03. **Addition with Ozone :**

Statement :



Benzene

Benzene triozonide

$$\xrightarrow[\text{(Zn-dust+steam)}]{\text{Hydrolysis}} 3\ \text{ZnO} + 3\ \begin{array}{l}\text{CHO}\\ |\\ \text{CHO}\end{array}$$

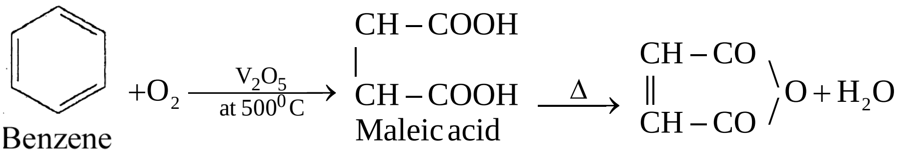
(glyoxal Ethanedial)

C. Oxidation :

i) Combustion : When benzene is heated with oxygen gives sootyflame along with CO_2, H_2O and heat. (sooty flame is due to unburnt carbons as the number of carbon atoms are more in comparision to hydrogen atom,)

$$2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O + \text{Heat.}$$

Statement :



$$\text{Benzene} + O_2 \xrightarrow[\text{at } 500^0\text{C}]{V_2O_5} \begin{array}{l}\text{CH}-\text{COOH}\\ |\\ \text{CH}-\text{COOH}\end{array} \xrightarrow{\Delta} \begin{array}{l}\text{CH}-\text{CO}\\ \|\\ \text{CH}-\text{CO}\end{array}\!\!\!\!\begin{array}{l}\backslash\\ \\ /\end{array}\!\! O + H_2O$$

Benzene

Maleic acid

Maleic anhydride.

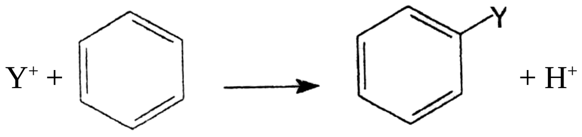
Uses :

01. Benzene is used as nonpolar solvent.
02. It is used in the preparation of other benzene derivatives.
03. It is used in dry cleaning.

L-118

Eletrophile is either a +vely charged ion or electrically deficient molecules and attack a place or react where there is more electron density.

When benzene is subjected to electrophillic substitution, only one monosubstituted product is formed since all the six positions of benzene are equivalent.



But when the monosubstituted benzene is further subjected to electrophillic substitution, three different products are formed. They are :

i) Ortho-disubstituted product (Relative positions 1:2 or 1 : 6).

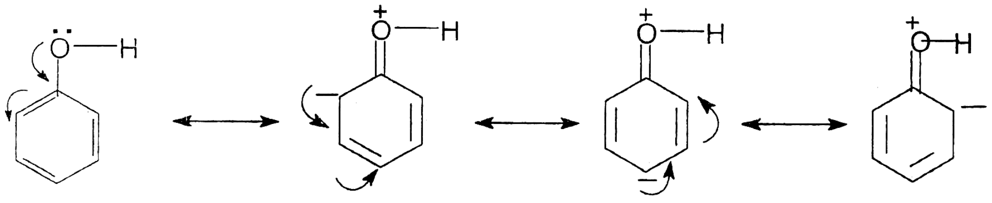
ii) Meta - disubstituted product (Relative positions 1 ; 3 or 1 : 5).

iii) Para - disubstituted product (Relative position 1 : 4).

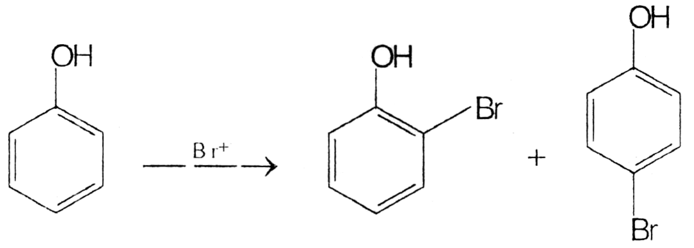
It is observed that nature of the substituent in monosubstitued benzene decides the formation of disubstituted product.

i) Some groups like -OH, $–NH_2$, $–CH_3$, –X etc. if already present forms o- and p- disubstituted products.

These groups are called activating groups and they pushes electrons in to the aromatic nucleus and the electron density increases at o-and p-positions as follows.

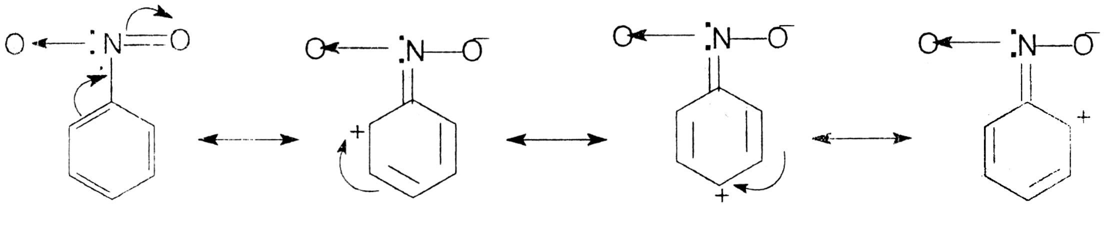


Since the electron density is more at o– and p- positions, the second electrophile will react either at o– positions or at p- position or both.

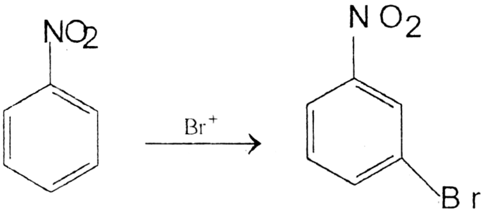


iii) Some groups like $–NO_2$, –CHO, –COOH, –COOR etc. direct the second electrophile to m-position. These groups are known as deactivating group and they withdraw electrons from o– and p- positions. Therefore m-position is comparatively more electron denser than O– and p-positions.

For example :



These groups are m-orienting groups because they increase the electron density at m-position but they decrease the electron density at both O– and P-positions.



HOME ASSIGNMENT

(a) How can you prepare p-chloronitrobenzene and o-ochloro nitrobenzene starting from benzene ?

(b) Convert the following :

Benzene $\longrightarrow$ Toluene

Toluene $\longrightarrow$ Benzene

Benzene $\longrightarrow$ Phenol

Phenol $\longrightarrow$ Benzene

Acetylene $\longrightarrow$ benzene

Benzene $\longrightarrow$ acetylene

Acetylene $\longrightarrow$ propyne,

Acetylene $\longrightarrow$ But-1-yne

Acetylene $\longrightarrow$ But-2-yne

(c) Show that benzene is an aromatic compound.

UNIT - XIV

ENVIRONMENTAL CHEMISTEY

L-119, L-120

Inroduction :

→ Living organism and surrounding in which it lives.

i.e. air, water, soil, sunlight, food which are basic needs of all organism (Living bodies) to survive

→ **Components of environment :**

(a) Abiotic or nonliving components

(i) Atmosphere or air (ii) Hydrosphere (water)

(iii) Lithosphere or rock and soil.

(b) Biotic or living components comprising of flora md fauna.

(c) Energy components : Solar, geothermal, nuclear etc.

→ **Significance :** 1972 united Nations conference on Human Environment held at stockholn alramed the environment pollution. The studies enlighten the people about importance of protection and conservation of environment & the need to restrain human activities leading to indiscriminate release of pollutants into the environment.

→ **Environmental pollutants :**

(i) **Gaseous air pollutants -** CO, SO_2, oxides of N, Halogens, H_2S, hydrocarbon, ozone & other oxidants.

(ii) **Particulate pollutants -** dust, mist, fumes, smoke, smog etc.

(iii) Metals - Hg, Pb, Zn, Fe, Ni, Sn, Cd, Cr etc.

(iv) Organic substance - Ether, benzene, acetic acid

(v) Agrochemicals - fertilisers & biocides (pesticides funcgicides, nematicides, bacteriacides.

(vi) Radioactive waste

(vii) Noise

* AIR POLLUITON

1. Gaseous air pollutant :

(a) Oxides of sulfur - origin : Roasting of ore, burning of fossil fuel.

It is poisonous to both animals and plants. Even low concentration of SO_2 causes respiratory diseases (asthma, bronchitis.....)

$$SO_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow SO_{3(g)}$$

Such reaction in air catalysed by particulates & promoted by ozone and hydrogen peroxide.

$$SO_{2(g)} + O_{3(g)} \longrightarrow SO_{3(g)} + O_{2(g)}$$

$$SO_{2(g)} + H_2O_{2(g)} \longrightarrow SO_{3(g)} + H_2O \longrightarrow H_2SO_{4(aq)}$$

(b) Oxides of Nitrogen

$$N_{2(g)} + O_{2(g)} \xrightarrow{1483K} 2\,NO_{(g)}$$

During lightening in atmosphere, burning of fossil fuels

$$NO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow NO_{2(g)}$$

It is faster in presence of ozone

$$NO + O_3 \longrightarrow NO_2 + O_2$$

Effect : * High concentration of NO_2 damage leaves

* Retard rate of Photosynthesis

* Lung irritant causing respiratory disease in children.

* Harmful to various textile fibres & metals.

(c) Hydrocarbon : Produced in incomplete combustion of automobile fuel.

Effect : * These are carcinogenic.

* Harm plants by caussing ageing, shedding leaves, flowers, twigs.

(d) Oxides of carbon :

(i) CO produced by incomplete combustion of carbon (coal, coke), automobile exhaust

Effect : * Formation of carboxy haemoglobin to creat oxygen deficiency resulting headache, weak eye sight, nervousness and cardiovascular disorder, premature birth, deformed baby.

(ii) CO_2 : buring fossil fuel, decomposition of limestone (cement factory), vulcanic eruption. It is confined to troposphere (0.03% CO_2). Green plant used CO_2 for photosynthesis emitting oxygen maintaining a balance in nature.

Effect : CO_2 in air is mainly responsible for **global warming.**

* **Harmful effect of air pollution :**

(a) Global warming green-hous effect : The temperature on the surface of the earth is maintained by energy balance between sunreys striking the earth and heat radiated back into the outer space. Increased concentration CO_2 forms a glass panal of green house. It absorbs sunrays but preevents the heat being irradiated to outer space. Such a phenomenon results in heating up of earth's atmosphere. This effect is called **green house effect.**

Green house gases : CH_4 (form paddy fields, rotting garbase dumps,) fossid fuels), CFC (Industrial chemical used in air conditioning), water vapour, nitrous oxide, ozone)

Effect : * increase of global temperature.

* Melting of polar ice caps.

* flooding of low lying areas all over earth

* Increase of infectious disease like dengue, malaria, yellow fever, sleeping sickness etc.

(b) Acid rain : Dissolved oxides of nitrogen, sulfur when the pH of the rain water drops belo 5.6 causes acid rain.

$$2SO_{2(g)} + O_{2(g)} + 2H_2O(l) \rightarrow 2H_2SO_4(aq)$$

$$4\ NO_{2(g)} + O_{2(g)} + 2H_2O(l) \rightarrow 4\ HNO_3(aq)$$

60 - 70% of acidity is attributed due to H_2SO_4 where as 30-40% by HNO_3.

Impacts : Decrease of pH affect aquatic life, production of crops, monuments (Tajmahal is affected by Mathura Refinery), bridges, statues, railings etc.

* Levels of heavy metals like Al, Mn, Zn, Cd, Pb, Cu in water getting increased beyond safe limit.

* Useful bacteria & blue green algae are destroyed due to acidification causing ecological imbalance.

2. **Particulate Pollutant :** Minute solid particles, vehicle emission, smoke particles from fire, ash from industries, living micro organisms, bacteria, fungi, moulds, algae etc.

(i) **Smong : (smoke + fog)**

(a) Reducing smog (smoke + fog + SO_2)

(b) Photo chemical smog occurs in warm, dry and sunny climate. It results from action of sunlight on unsaturated hydrocarbon and nitrogen oxides. Due to high concentration of oxidising agents, this called oxidising smog.

$$NO_{2(g)} \xrightarrow{hv} NO_{(g)} + O_{(g)}$$

$$O + O_2 \longrightarrow O_{3(g)}$$

$$NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)}$$

O_3 is toxic gas and both NO_2 and O_3 are strong oxidising agent.

$$3CH_4 \quad + \quad 2O_3 \longrightarrow \quad 3HCHO + 3H_2O$$

Unburnt hydrocarbon

$CH_2 = CH - CHO$ (acrolein), $CH_3(CO)OONO_2$

peroxyacetyl nitrate (PAN)

Effect : (i) Both O_3 and PAN are eye irritant.

(ii) O_3 and NO irritate nose, throat ; headache chest pain, breathing problem

(iii) Corrosion of metals, stones, building materials rubber, painted surface.

Prevention :

(i) Using catalytic converters in automobiles preventing release of nitrogen oxide & hydrocarbon.

(ii) Plantation of pinus, Juriparus, vitiy that can metabolise Nitrogen oxide.

* Ozone depletion : (stratopheric pollution)

Ozone layer protects the harmful U.V. radration (causing melanoma, i.e. skin cancer)

$$O_{2(g)} \xrightarrow{UV} O_{(g)} + O_{(g)}$$

$$O_{(g)} + O_{2(g)} \rightleftharpoons + O_{3(g)}$$

CFC, main reason for ozone layer depletion.

$$CF_2Cl_{2(g)} \xrightarrow{h\nu} Cl + CF_2Cl_{(g)}$$

$$.Cl_{(g)} + O_{3(g)} \longrightarrow ClO._{(g)} + O_{2(g)}$$

$$ClO._{(g)} + O_{(g)} \longrightarrow Cl_{(g)} + O_{2(g)}$$

.Cl breaks down ozone.

→ Ozone hole – Depletion of ozone layer is called ozone hole, observed in 1980 over south pole.

→ During Winter - Stratospheric cloud on its surface chlorine nitrate formed.

$$ClO._{(g)} + NO_{2(g)} \longrightarrow ClONO_{2(g)}$$

$$.Cl_{(g)} + CH_{4(g)} \longrightarrow .CH_{3(g)} + HCl_{(g)}$$

$$ClONO_{2(g)} + H_2O_{(g)} \longrightarrow HOCl_{(g)} + HNO_{3(g)}$$

$$ClONO_{2(g)} + HCl_{(g)} \longrightarrow Cl_{2(g)} + HNO_{3(g)}$$

→ During spring on return of sunlight (spring), breaks up cloud & HOCl and Cl_2 are photolysed by sun light.

$$HOCl_{(g)} \xrightarrow{h\nu} .OH + .Cl_{(g)}$$

$$Cl_{2(g)} \xrightarrow{h\nu} 2Cl.$$

Chain continues to deplete ozone.

Effect : (i) Skin diseases

(ii) Killing phytoplanktons, damage to fish productivity.

(iii) Decreases the moisture content of the soil.

(iv) Damage to paint and fiber

All these are due to entering of U.V. radiation into troposphere.

* **Water pollution :**

→ **Chief sources of water pollution.**

(a) Sewage & other wastes.

(b) Industrial waste (organic wasts & chemical pollutants)

(c) Agriculture discharges (Fertilisers and pesticides)

(d) Radioactive waste (Nuclear arm tests ^{90}Sr & ^{137}Cs

(e) Thermal pollution

(f) Oil pollution (spilling of oil during transport)

→ Effects of water pollution

(i) Human and animal wealth (metal poisoning)

(ii) Loss of recreational areas.

→ Prevention and control of water pollution

(i) Stabilisation of ecosystem (Reduction of waste input etc.)

(ii) Reutilisation, recycling waste-(Treatment of muncipal and industrial waste)

(iii) Removal of pollutants (Adsorption, electrodialysis, ion exchange reverse osmosis etc for purification of water)

CSIR has developed different techniques for different pollutants such as NH_3, Hg, Phenolics, colouning matter, sodium salts.

* **SOIL POLLUTION :**

→ **Sources of soil pollution -**

(i) Industrial water -

(ii) Urban waste -

(iii) Agriculture waste - (Fertiliser and pesticides)-

* Farm waste (From diaries, poultries..........

(iv) Radioactive waste

(v) Pollution by biological agents (excreta, sewage...............

(vi) Clinical waste (Form hospitals, clinics..................

→ Causing health hazards, ecological imbalance ....

* **Green Chemistry** as an attractive tool for reducing pollution :

Green chemistry is defined as the sustainable, safe and non-polluting chemical science which enables man to manufacture products with minimum consumption of materials and energy and also production of minimum waste.

→ Use of environment friendly reagents :

(i) Use of sunlight and microwave.

(ii) Use of sound waves (sono chemistry)

(iii) Use of enzymes

→ Achievement of green chemistry :

(i) Replacement of organtins by 'Sea nine' as antifouling compound in sea marines.

(ii) Replacement of CFC, by CO_2 as blowing agent. Suspected carcinogen, $Cl_2C = CCl_2$ used in dry cleaning now replaced by liquefied CO_2 with suitable detergent. Ecofriendly H_2O_2 can be used for bleaching purpose.

(iii) Synthesis of ethanol from ethene -

$$CH_2 = CH_2 + O_2 \xrightarrow[\text{Pd(II)/Cu(II)in water}]{\text{Catalyst}} CH_3CHO(90\%)$$

Thus green chemistry in nutsheel, is a cost effective approach which involve reduction in material, energy consumption and waste generation.

HOME ASSIGNMENT

(a) Fill in the gaps :

(i) Ozone is present in ____________ region of the atmosphere.

(ii) ______ is mainly responsible for ozone layer depletion.

(iii) In absence of ozone layer _______ rays enter in to the atmosphere.

(iv) ________ gas removes oxygen from oxyhaemoglobin.

(v) The national monument now affected badly by acid rain is ____________ .

(b) Choose the correct answer :

(i) Which gas is not involved in the formation of photo chemical smog ?

(a) NO (b) Hydrocarbon (c) SO_2 (d) O_3

(ii) Which of the following is not a green house gas ?

(a) CO_2 (b) CH_4 (c) CFC (d) O_2

(iii) Which of the following radicals reacts with ozone ?

(a) Cl. (b) ClO. (c) $.CH_3$ (d) .OH

(iv) Which of the following is not an oxidant ?

(a) SO_2 (b) O_3 (c) NO_2 (d) None of these

(v) Which of the following is not a gaseous pollutant?

(a) SO_2 (b) H_2S (c) CO (d) fume

(c) Write notes on -

(i) Green house effect (ii) Ozone layer depletion

(iii) smog (iv) BOD (v) Acid rain

(d) Discuss the different sources of water pollution.

◆◆◆

CLASS - XII

Contents

CHEMISTRY

LESSON PLAN – 2018-19

(2nd Year /Class XII)

Unit	Lect. No.	Topic	Date of Completion
I	**SOLID STATE**		
	L-1	Classification or solids based on differend binding forces: molecular, ionic, covalent and metallic solids (elementary idea only). Amorphous solids and Crystalline solids.	
	L-2	Unit cell and types of unit cell, unit cell in two dimensional and three dimensional lattices.	
	L-3	Calculation of density of unit cell and numericals.	
	L-4	Packing in solids, Packing efficiency, voids number of atoms per unit cell in a cubic unit cell.	
	L-5	Point defects (Both stoichiometric & Non stoichiometric defect)	
	L-6	Electrical and magnetic properties, Band theory to explain electrical properties, n & p type semiconductor and applications.	
II	**SOLUTIONS**		
	L-7	Types of solutions, expression or concentration of solutions of solids in liquids with numericals	
	L-8	Solubility, Solubility of gases in liquids (HENRY'S LAW) and solid solutions	
	L-9	Colligative properties - relative lowering of vapour pressure, Raoult's law and numerical	
	L-10	Elevation of boiling point and numericals, Depression in freezing point and numericals	
	L-11	Osmosis, Osmotic pressure, isotonic, hypertonic and hypotonic solutions.	
	L-12	Determination of molecular masses using colligative properties and Abnormal Colligative properties with problems	
	L-13	van't Hoff factor, Azeotropes, types of Azeotropes	
	L-14	Ideal solution, Non-ideal solution, Non ideal solution showing +ve and -ve deviations with examples.	
III	**ELECTROCHEMISTRY**		
	L-15	Electrolyte and non electrolyte Electronic conductors and ionir conductors, strong electrolyte, weak electrolyte	
	L-16	Variation of conductivity with concentration, Electrolysis and causes of electrolysis (Faraday's laws of electrolysis)	
	L-17	Conductance, Resistance, Conductivity, resistivity and numericals	

	L-18	Molar conductance, Equivalent conductance, Kohlraausch's law, numerical and application.	
	L-19	Redox reactions, Galvanic cell or Voltaic cell or Electrochemical cell. Dry cell, Lead accumulator.	
	L-20	EMF of a cell, standard electrode potential with numericals	
	L-21	Electrochemical series and its application, Nernst equation and its application to chemical cells	
	L-22	Relation between ∆G and cell potential, equilibrium constant, corrosion, Fuel cell: Hydrogen - oxygen fuel cell and its advantages.	
IV	**CHEMICAL KINETICS**		
	L-23	Rate of a reacion (Average and instantaneous rate of reaction)/ factors affecting the rate of reaction, Numerical based on rate of reaction, rate law and specific rate constant.	
	L-24	Order and molecularity of a reaction, Difference between molecularity and order of reaction, Difference between rate of reaction & -specific rate of reaction.	
	L-25	Integrated rate expression for zero order and first order reaction with half life period.	
	L-26	Concept of collision theory (elemenary idea only) activation energy, Activated complex.	
	L-27	Arrhenius equation and determinatin of activation energy, Significance of activation energy, Graphical analysis of 1st order reaction	
V	**SURFACE CHEMISTRY**		
	L-28	Adsorption : Adsorbate, Adsorbent, desorption, types of adsorptions (physisorption and chemisorption), Factors affecting adsorption of gases on solids and its application	
	L-29	Catalysts, catalysis, types of catalysts, (Homogeneous and hetero geneous catalysis) enzyme catalysis, Activity of a solid catalyst, selectivity of a solid catalyst.	
	L-30	Colloidal state, Colloids, Distinction between true solution, colloids and suspensions properties of solloids: Tyndall effect, Brownian movement	
	L-31	Electrophoresis,. coagulation, emulsion - types of emulsions, colloidal system based on Lyophilic solutions, lyophobic solutions multimolecular and mcromolecular colloids	
INORGANIC			
VI	**GENERAL PRINCIPLES & PROCESSES OF**		
	L-32	Metallurgy, Principles and methods of extraction: Crushing and Grinding, Concentration of ore, Leaching process, Calcination & roasting (Oxidation), Reduction, electrolytic method and refining	

	L-33	Occurrence and principles of extraction of Aluminium, Ellingham diagram	
	L-34	Occurrence and principles of extraction of Copper	
	L-35	Occurrence and principles of extraction of Zinc	
	L-36	Occurrence and principles of extraction of iron	
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	L-37	General introduction, electronic configuration, occurrence, Oxidation states, General trends in physical and chemical properties	
	L-38	Nitrogen preparation, properties and uses, Compounds of nitrogen	
	L-39	Preparation, properties and uses of ammonia and nitric acid, Oxides of nitrogen (Structure only)	
	L-40	Allotropic forms of phosphorous compounds of phosphorous, preparation, properties and uses of phosphine, Halides (PCl_3, PCl_5), Oxoacids (elementary idea only)	
	GROUP-16 Elements		
	L-41	Genera! introduction. Electronic configuration, Occurrence, Oxidation states. General trends in physical and chemica! properttes	
	L-42	Preparation, properties and uses of dioxygen, Classification of oxides	
	L-43	Preparation, properties and uses of ozone, structure of Ozone	
	L-44	Preparation, properties and uses of SO_2, H_2 SO (industrial process of Manufacture), Oxoacids of sulphur (Structure only)	
	GROUP-17 Elements		
	L-45	General introduction, occurrence, electronic configuration, oxidation state, General trends in physical and chemical properties	
	L-46	Compounds of halogen, preparation, properties, uses of chlorine, preparation, properties, uses of HCl	
	L-47	Interhalogen compounds, oxoacids of halogens (Structure only)	
	GROUP-18 Elements		
	L-48	General introduction, electronic configuration, Occurrence, General trends in physical and chemical properties.	
	L-49	Uses of noble gases, Structure, ppreparation & properties of XeF_2, FeF_4 & XeF_6.	

VIII	**d & f BLOCK ELEMENTS**		
	L-50	General introduction, Electronic configuration, Occurrence, why the d-bock elements called transition elements ? Characteristics of transition element. General properties of the transition element or first row transition metals. (metallic character, ionisation enthalpy)	
	L-51	Oxidation state, ionic radii, colour catalytic property, magnetic properties, formation of interstitial compounds, alloy formation	
	L-52	Preparation and propeties of $K_2Cr_2O_7$ & $KMnO_4$ with uses	
	L-53	Electronic configuration of Lanthanoids, Oxidation states. Chemical reactivity, Lanthanoids contraction and its consequences	
	L-54	Electronic configurations, oxidation states, Occurrence of actinoids, comparative study of lanthanoids and actinoids	
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	L-55	Introduction : Double salts, Ligands, co-ordination number & Shapes	
	L-56	Werner’s theory & it’s illustrations.	
	L-57	IUPAC nomenclature of ‘ mononuclear co-ordination compounds	
	L-58	Structural & Stereo isomerism	
	L-59	VBT	
	L-60	CFT	
	L-61	Importance of co-ordination compounds (In qualitative analysis/ Extraction of metals and biological system)	
ORGANIC			
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	L-63	Preparation of haloalkane and physical properties, Chemical properties	
	L-64	Mechanism of Nucleophillic substitution reaction (SN2 and SN1), optical rotation	
	L-65	Haloarenes/ nomencsature and nature of C–X bond, Substitution reaction (directive-influence of halogen monosubstituted compounds only)	
	L-66	Uses and environmental effects of CH_2Cl_2, $CHCl_3$, CCl_4, CHI_3, CF_2Cl_2, DDT, BHC	
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	L-67	Classificatin of alcohols, nomenclature, Methods of preparation of alchols, physical properties	
	L-68	Chemical properties (1^0–Alcohol only)	

	L-69	Identificaton of 1^0, 2^0, 3^0, Alcohols, mechanism of dehydration	
	L-70	Uses of methanol and ethanoi, nomenclature of phenols, Methods of preparation of phenols	
	L-71	Physical and Chemical properties of phenol	
	L-72	Acidic nature of phenol electrophilic substitution reaction and uses of phenol, Nomenclature of Ethers, Methods of preparation	
	L-73	Physical and Chemical properties of Ethers and uses.	
XII	**ALDEHYDES, KETONES AND CARBOXYLIC**		
	L-74	Introduction. Different methods of preparation of aliphatic aldehydes and ketones	
	L-75	preparation of Aldehyde only. Properties of aldehyde and ketone (start)	
	L-76	Properties of Aldehydes and Ketones (comp.)	
	L-77	Distinction between aldehydes and ketones. Distinction between acetaldehyde and formaldehyde	
	L-78	Aromatic aldehyde : Preparation and properties (start) of benzaldehyde	
	L-79	Properties of benzaldehyde(comp.)	
	L-80	Monocarboxylic acids : Introduction, different methods of preparation, physical properties	
	L-81	Comparision of acid strength and chemical properties of monocarboxylic. acid. Distinction between formic acid and acetic acid	
	L-82	Preparation and properties of benzole acid (aromatic acid).	
XIII	**ORGANIC COMPOUNDS CONTAINING**		
	L-83	Aliphatic amines : Introduction, preparation and basic character of aliphatic amines	
	L-84	Properties of aliphatic amines and preparation of aniline. Basic character of aniline	
	L-85	Properties of aniline	
	L-86	Preparation and and properties of benzene diazonium chloride (BDC)	
	L-87	Interconversion of organic compounds	
XIV	**BIOMOLECULES**		
	L-88	Carbohydrates : Introduction, nomenclature. D,L-configuration of fructose oligosaccharides (sucrose, lactose and maltose) polysaccharides (starch, cellulose, glycogen.	
	L-89	Proteins, amino acids, Peptide bond or peptide linkage, Structure of proteins & Denaturation protein.	
	L-90	(A) Hormones(enzymes) only elementary idea (excluding structure). (B) Vitamins types and functions.	
	L-91	Nucleic acids (DNA & RNA)	

XV	**POLYMERS**		
	L-92 & L93	Classification : types of polymerisation, monomer(s) and uses of different polymers such as : (1) polythene (2) PVC (3) neoprene (4) Reflon (5) Buna-s (6) Nylon-6 (7) Nylon-66 (8)Bakelite (9) PAN (10) polythene (11) Buna (12) Terylene	
XVI	**CHEMISTRY IN EVERYDAY LIFE**		
	L-94, L-95 & L96	A. Chemicals as medicine, (1) Antipyretics (2) Analgesis (3) Antiseptics (4) Antibiotics (5) Antacids (6) Anti histamines (7) Tranqualizers (8) Disinfectants (9) Antifertility drugs (1) Anti microbials. B : Chemicals in food (1) Antificial sweeting agents (2) Preservatives (3) Elementary idea reagarding antioxidants (4) soaps and detergents and their cleansing action.	

Lecture -1

UNIT - I
SOLID STATE

The characteristic properties of silids are :

- (i) They have definite mass, volume and shape
- (ii) Intermolecular distance between the constituent particles are short
- (iii) Intermolecular forces of the attraction is strong
- (iv) Their constituent particles (atoms, molecules or ions) have fixed positions and can only oscillate about their mean positions
- (v) They are incompressible and rigid
- (vi) They have high melting point

Classification of Solids : On the basis of order of arrangment of the constituent particles is solids, they are of two types i.e. amorphous and crystalline solids.

Crystalline Solids : Crystalline solids are rigid and icompressible, and there is ordered arrangement of constituent particles (atoms, molecules or ions). They have definite shape have sharp melting point, and they are arisotropic.

Example- Sodium chloride, alum, quartz. In sodium chloride Na^+ and Cl^- ions are arranged in crystal lattice at alternate sites. Each Na^+ ion is sorrounded by six Cl^- ions and each Cl^- ion is sorrounded by six Na^+ ion.The shape of NaCl crystal is cubic.

Some crystalline solids containg water of crystallization are, Blue vitriol ($CuSO_4$, $5H_2O$), Green vitriol ($FeSO_4$, $7H_2O$), White vitriol ($ZnSO_4.7H_2O$) Potash Alum (K_2SO_4, Al_2 $(SO_4)_3$, $24H_2O$).

Amorphous Solids : Amorphous solids are rigid and incompressible, but in these solids the arrangement of constituent particles (atoms, molecules or ions) has only short range order. They are isotropic.

Example : Glass, rubber, plastic.

The amorphous solids have no sharp melting point, they soften over a range of temperature.

Classification of Crystaline Solids

On the basis of nature of intermolecular forces the crystalline solids are of the following types.

(a) Molecular Solids : In molecular solids, the constituent particles are molecules. They are subdivided into following types

- (i) Non-polar molecular solids - These solids contain either atoms like argon and helium or molecules formed by non-polar covalent bonds. For example H_2, Cl_2 and I_2. In these solids the molecules are held by weak dispersion forces or London-forces.
- (ii) Polar molecular solids- The molecules of substances like HCl, SO_2 are formed by polar covalent bonds. The molecules are held together by relatively stronger dipole-dipole interactions.
- (iii) Hydrogen bonded molecular solids - In these solids the molecules are held together by hydrogen bonds between H and F, O or N atoms. Example - H_2O(ice)

(b) **Ionic solids -** In ionic solids the constituent particles are ions and they are held together by strong electrostatic foces of attraction. These solids are hard & brittle they have high m.p. and b.p. They donot conduct electricity in the solid state but do so in molten state or in aqueous solutions.

(c) **Metallic solids :** In metallic solids, the constituent particles are positive ions immersed in a sea of free electrons. These electrons are mobile and are responsible for high electrical and thermal conductivity of metals. These solids are malleable, ductile, and have lustre.

(d) Covalent Solids- In covalent solids the constituent particles are atoms which are held together by covalent bonds. The bonds in covalent solids extend throughout the crystal and this results in the formation of a giant three dimensional structure. Such solids are hard and brittle. They have extremely high m.p. They are insulators and do not conduct electricity.

Example- Diamond, Silicon carbide, Graphite.

Lecturer : 2

Crystal lattice - In a crystal the regular three dimensional arrangement of points (atoms, molecules or ions) in space is called crystal lattice.

(i) Each point in a crystal lattice represents one constituent particle.

(ii) Lattice points are joined by straight lines to bring out the geometry of the lattice.

Unit Cell : Unit cell is the smallest portion of the crystal lattice which, when repeated in different directions generates the entire lattice.

A unit cell is characterised by (i) its dimensions along the three edges a, b and c. (ii) angles between the edges, α (between b and c), β (between a and c), γ (between a & b). Thus a unitcell is characterised by six parameters, a, b, c, α, β and γ.

Types of unit cells : These are of two types

(a) Primitive unit cells - In it the constituent particles are present only on the corners of a unit cell. These are of different types.

(b) Centred unit cell - In it in addition to the corners, one or more constituent particles are present at positions other than the corners.

Centred unit cells are of three types :

(i) Body-centred unit cells - In such unit cell one constituient particle (atom, molecular or ion) in present in its body-centre besides the ones that are present at its corners.

(ii) Face-centred unit cells - In such unit cell, one constituent particle is present at the centre of each face besides the ones present at its corners.

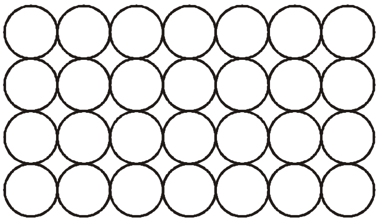
(iii) End-Centred unit cells - In such unit cell, one constituent particle is present at the centre of any two opposite faces besides the ones present at its corners.

Close packing Crystalline Solids

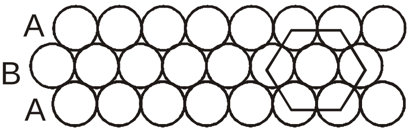
Letus consider the constituent particles as identical hard spheres and build up three dimensional structure as follows.

(a) **Close packing in two dimensions** Two dimensional close packed structure can be generated by placing the rows of close packed structure in the different ways.

(i) Square close packing - In this case, the second row is placed in contact with the first one, in such a way that the spheres of the second row are exactly above those of the first ow. The spheres of the rows are aligned horizontally and vertically.



Square close packing



Hexagonal close packing

(a) square close packing of spheres in two dimensions.

(b) hexagonal close packing of spheres in two dimension

(ii) **Hexagonal close packing of spheres.** In this type of packing the spheres are packed in such a way that the spheres of the second row are placed on the depressions between the spheres of the first row. similarly the spheres of the third row are placed in the depressions between the spheres of second row and so on.

(b) **Close packing in three dimensions.** The three dimensional structures are obtained by stacking two dimensional layers one above the other. These are of two types.

(i) **Three dimensional close packing from two dimensional square close-packed layers:**

The second layer is placed over the first layer such that the spheres of the upper layer are exactly above those of the first layer. In this arrangement spheres of both the layers are perfectly aligned horizontally as well as vertically. Similarly we may place more layers one above the other. If the arrangement of spheres in the first layer is called A type, all the layers have the same arrangement. Thus this lattice has AAA. type pattern.

The lattice thus generated is the simple cubic lattice and its unit cell is the primitive cubic unit cell.

(ii) **Three-dimensional clse packing from two dimensional hexagonal close packed layers.**

Three dimensional close packed structure can be generated by placing layers one over the other.

(a) **Placing second layer over the first layer.** Let us take a two dimensional hexagonal close packed layer ‘A’ and place a similar layer above it such way that the spheres of the second layer are placed in the depression of the first layer. Let us call the second layer as ‘B’. It can be observed from the figure that not all the triangularvoids of the first layer are covered by the spheres of the second layer. This gives rise to different arrangements. Whenever the spheres of the second layer is above the voids of the first layer (or vice versa) a tetrahedral void is informed. These voids are called tetrahedral voids because a tetrahedron is formed when the centres of these four spheres are joined. They have been marked s ‘T’.

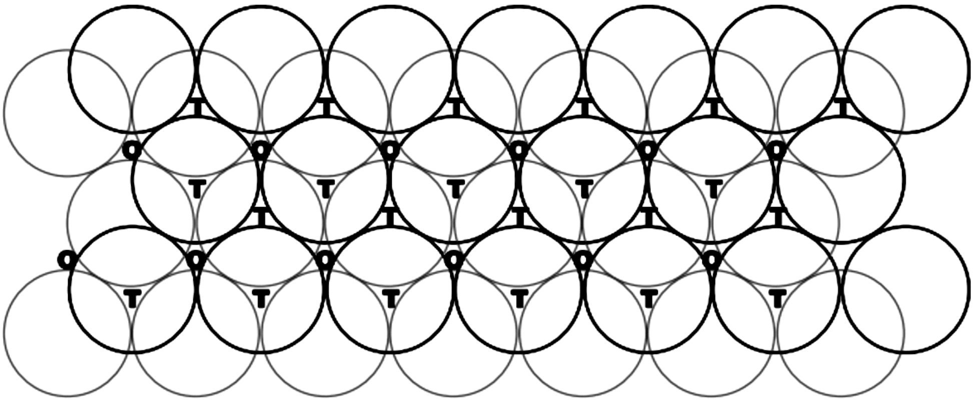
At other places, the triangular voids in the second layer are above the triangular voids of the first layer and the triangular shapes of these donot overlap. One of them has the apex of the triangle pointing upwards and the other downwards.

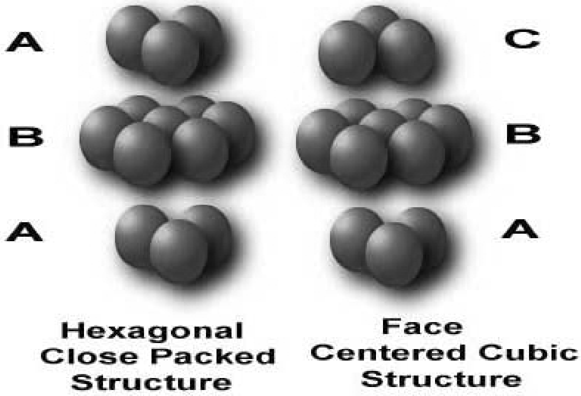
These voids have been marked ‘O’ in the figure. Such voids have been sorrounded by six spheres and are called octahedral voids.

(b) Placing third layer over the second layer.

(i) When the third layer is placed over the second layer in such a way that the spheres cover the tetrahedral voids, a three dimensional close packing is obtained where the spheres in every third or alternate layers are vertically aligned i.e. the third layer is directly above the first and the fourth layer is above the second layer and so on. Calling the first layer as layer A and second layer as layer B, the arrangement is called ABAB... pattern or hexagonal close packing (hcp). This type of packing is seen in case of molybdenum, Magnesium and Beryllium.

(ii) When the third layer placed over the second layer in such a way that spheres cover the octahedral voids, a layer different from A and B is produced. Let us call it as layer ‘C’. Continuing further a packing is obtained where the spheres of every fourth layer will be vertically aligned. This pattern of stacking spheres is called ABCABC...... pattern or cubic close packing (ccp)





Lecture - 3

Calculation density unit of a Cubic Crystal from its Edge.

Case I : For Cubic crystals of elements :

Suppose the edge of the unit cell = a pm

No. of atoms present per unit cell = Z

Atomic mass of the element = M

Volume of the unit cell = $(\text{a pm})^{43}$

$$= \left(\text{a} \times 10^{-10}\,\text{cm}\right) = \text{a}^3 \times 10^{-30}\,\text{cm}^3$$

Density of the unit cell $= \dfrac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$ .... (1)

Mass of the unit cell = No. of atoms in unit cell × Mass of each atom

$= \text{Z} \times \text{m}$

m = Mass of each atom $= \dfrac{\text{Atomic mass}}{\text{Avogaro's number}} = \dfrac{\text{M}}{\text{N}_0}$

Substituting this value is equation (1), we get

$$\text{Density of unit cell} = \frac{\text{Z} \times \dfrac{\text{M}}{\text{N}_0}}{\text{a}^3 \times 10^{-30}}$$

i.e., $\boxed{\text{e} = \dfrac{\text{Z} \times \text{M}}{\text{a}^3 \times \text{N}_0 \times 10^{-30}}}$ .... (2)

Where 'a' is in pm and M is in g mol^{-1}

(ii) For ionic compounds of cubic crystal

The formula is same except that now Z is the number of formula unit present in one unit cell and is the formula mass

(i) If 'a' is in cm and M in g mol^{-1}, the equation (2) becomes

$$\text{e} = \frac{\text{Z} \times \text{M}}{\text{a}^3 \times \text{N}_0}\ \text{g}/\text{cm}^3$$

(ii) In S.I. units, M is Kg mol^{-1} and 'a' in metres, then

$$\text{e} = \frac{\text{Z} \times \text{M}}{\text{a}^3 \times \text{N}_0}\,\text{Kg}\,\text{m}^{-3}$$

(iii) For ionic compounds A^+B^- having fcc structure like NaCl

Edge (a) = 2 × distance between A^+ B^- ions

For conic compounds Z=number of formula units in one unit cell i.e. 4 for NaCl and Zns, 1 for CsCl.

M = Molecular mass of the compound.

N.B. For BCC structure of an element (like alkali metals)

Z = 2

For BCC structure of ionic compounds like CsCl, Z = 1

Numericals

1. Silver forms ccp lattice and X-ray studies of its crystal shows that the edge length of its unit cell is 408.6 pm. Calculate the density of silver (At mass of Ag = 107.9)

Ans. $\rho = \dfrac{Z \times M}{a^3 \times N_0}$

For ccp lattice (Which is equivalent to fcc lattice), Z = 4 atoms/unit cell

$$a = 408.6\text{ pm} = 408.6 \times 10^{-12}\,\text{cm}$$

$$\therefore \quad \rho = \frac{4\,\text{atoms} \times 107.9\,\text{g mol}^{-1}}{\left(408.6 \times 10^{-12}\right)^3 \left(6.022 \times 10^{23}\,\text{atoms mol}^{-1}\right)}$$

$$= 10.5\text{ g cm}^3$$

2. Sodium has bcc structure with neighbour distance 365.9 pm. Calculate its density.

Ans. For the bcc structure $d = \dfrac{\sqrt{3}}{2}a$

$$\text{or} \quad a = \frac{2}{\sqrt{3}}d = \frac{2}{1.732} \times 365.9 = \frac{2 \times 23\,\text{g mol}^{-1}}{\left(422.5 \times 10^{-10}\,\text{cm}\right)^3 \left(6.02 \times 10^{23}\,\text{mol}^{-1}\right)}$$

$$= 1.51\text{ g/cm}^3,$$

3. Gold (at mass 197), atomic radius = 0.144 nm, crystallizes in a pc face centred unit cell Determine the density of gold.

Ans. For fcc unit cell, $r = \dfrac{a}{2\sqrt{2}}$ or $a = 2\sqrt{2}r = 2 \times 1.414 \times .144\text{nm}$

$$= 0.47\text{nm} = 0.407 \times 10^{-7}\text{ cm}$$

$$\rho = \frac{Z \times M}{a^3 \times No} = \frac{4.197\,\text{g mol}^{-1}}{\left(0.407 \times 10^{-7}\text{cm}\right)^3 \times \left(6.02 \times 10^{23}\text{mol}^{-1}\right)} = 19.4\text{ g cm}^3$$

4. An element has body centred cubic (bcc) structure with a cell edge of 288 pm. The density of the element is 7.2 g/cm^3. How many atoms are present in 208 g the elements.

Ans. Volume of the unit cell = $\left(288\text{pm}\right)^3 = \left(288 \times 10^{-12}\text{m}\right) = \left(288 \times 10^{-10}\text{cm}\right)^3$

$$= 2.39 \times 10^{-23}\text{ cm}^3$$

Volume of 208 g of the element = $\dfrac{\text{mass}}{\text{density}} = \dfrac{208\,\text{g}}{7.2\,\text{g cn}^{-3}} = 28.88\,\text{cm}^3$

Number of unit cells in the volume = $\dfrac{28.88\,\text{cm}^3}{2.39 \times 10^{-23}\text{cm}^3/\text{unit cell}} = 12.08 \times 10^{23}$ unit cells

Since each cubic unit cell contains 2 atoms, the total number of atoms in 208 g = $2\left(\text{atoms/unit cell}\right) \times 12.08 \times 10^{23}$ units cells

$$= 24.16 \times 10^{23}\text{ atoms}$$

5. X-ray diffraction studies show that oopper crystallises in an fcc unit cell with-cell edge of 3.608×10^{-8} cm. In a separate experiment, copper is determined to have a density of 8.92 g/cm^3, Calculate the atomic mass of copper.

Ans. In case of fcc lattice, number of atoms per unit cell, Z=4 atoms

$$M = \frac{\rho N_0 a^3}{Z} = \frac{8.92\,g/cm^3 \times 6.02 \times 10^2 \text{ atoms mol}^{-1} \times \left(3.608 \times 10^{-8}\,cm\right)^3}{4\,\text{atoms}}$$

$$= 63.1 \text{ g/mol.}$$

$\therefore$ Atomic mass of copper is 63.1.

Lecture - 4

Number of atoms per unit cell of a cubic crystal system.

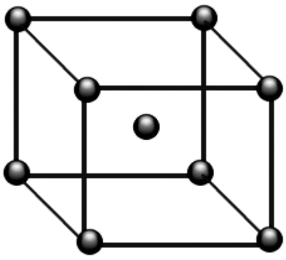
(i) **Simple primitive cubic unit cell.**

A simple cubic lattice has only 8 atoms on the corners. Each atom at a cormer is shared between 8 adjacent unit cells therefore only $\frac{1}{8}$ of an atom or molecule or ion actually belongs to a particular unit cell.

Since each cubic unit cell has 8 atoms on its corners, the total number of atoms in one unit cell is $8 \times \frac{1}{8} = 1$ atom.

(ii) **Body centred cubic unit cell (bcc)**

This lattice has 8 atoms at the corners and one atom at the body centre.



The atom at the body centre wholly belongs to the unit cell is which it is present.

Contribution by 8 atoms present on the corners = $\frac{1}{8} \times 8 = 1$atom

Contribution by the atom present at the body centre = 1 atom

$\therefore$ The total number of atoms per unit cell = 1 + 1 = 2 atoms

(iii) **Face - centred cubic unit cell :**

A face centred cubic (fcc) unit cell contains atoms at all corners and at the centre of all faces of the cube. Each atom located at the face centre is shared between two adjacent unit cells and so only $\frac{1}{2}$ of atom belongs to a unit cell.

(i) Contribution by 8 atoms present on the corners

$$= 8\,\text{corners atoms} \times \frac{1}{8}\,\text{atom per unit cell} = 8 \times \frac{1}{8} = 1\,\text{atom}$$

(ii) Contribution by 6 face centred atoms

$$= 6\ \text{face centred atoms} \times \frac{1}{2}\ \text{atom per unit cell} = 6 \times \frac{1}{2} = 3\,\text{atoms.}$$

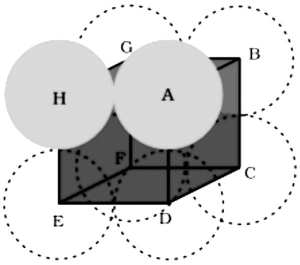
∴ Total number of atoms per unit cell = 1+3 = 4 arom.

Packing efficiency

The percentage of total space filled by the particles is called packing efficiency.

Calculation of packing efficiency.

(i) In a simple cubic lattice.



Suppose the edge length of the unit cell = a and radius of the sphere = r

As spheres are touching each other, a = 2r.

No of spheres per unit cell = $\frac{1}{8} \times 8 = 1$.

Volume of the sphere = $\frac{4}{3}\pi r^3$

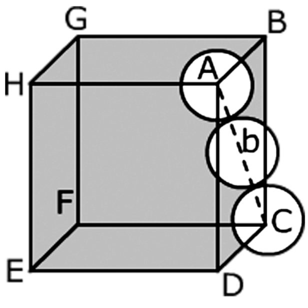
Volume of the cubic unit cell $a^3 = (2r)^3 = 8r^3$

∴ Packing efficiency = $\dfrac{\text{Volume of one atom}}{\text{Volume of the cubic unit cell}} \times 100$

$$= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100 = \frac{\pi}{6} \times 100 = 52.4\%$$

(ii) In face-centred cubic structure (Cubic close packing)

(fcc) (ccp)



The sphere on the centre is touching the spheres at the corners

So AC = r + 2r + r = 4r

In the right angled triangle ABC

$$AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}a$$

$$\therefore \quad \sqrt{2}a = 4r \quad \text{or} \quad a = \frac{4}{\sqrt{2}}r$$

Volume of the unit cell $= a^3 = \left(\frac{4}{\sqrt{2}}r\right)^3 = \frac{32}{\sqrt{2}}r^3$

No. of spheres in the unit cell = $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$.

So volume of four spheres = $4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$

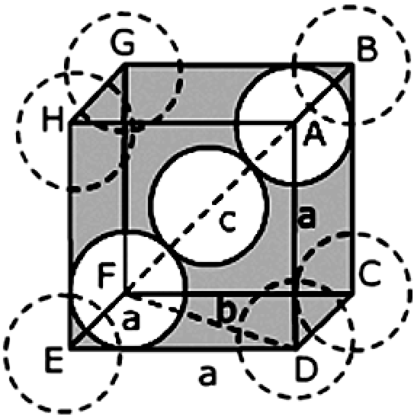
$$\therefore \quad \text{Packing efficiency} = \frac{\text{Volume occupied by four spheres in the unit cell}}{\text{Total volume of the unit cell}} \times 100$$

$$= \frac{16\pi r^3/3}{32r^3/\sqrt{2}} \times 100$$

$$= \frac{\pi\sqrt{2}}{6} \times 100 = 74\%$$

(iii) **In body-centred cubic structure.**

As the sphere at the body centre touches the spheres at the corners, the body diagonal AD = 4r



The face diagonal, $AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}a$

Body diagonal AD = $\sqrt{AC^2 + CD^2} = \sqrt{2a^2 + a^2} = \sqrt{3}a$

$$\therefore \quad \sqrt{3}a = 4r \quad \text{or} \quad a = \frac{4r}{\sqrt{3}}.$$

Volume of the unit cubic cell = $a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3 = \frac{64r^3}{3\sqrt{3}}$

No. of spheres per unit cell = $\left(8\times\frac{1}{8}\right)+1=2$

So volume of two spheres = $2\times\frac{4}{3}\pi r^3 = \frac{8}{3}\pi r^3$

$\therefore$ Packing efficiency = $\frac{\text{Volume occupied two spheres in the unit cell}}{\text{Total volume of the unit cell}}$

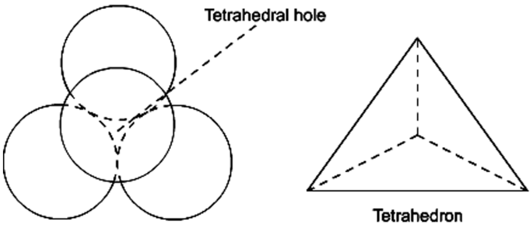
$$= \frac{8/3\pi r^3}{\left(\frac{64\ r^3}{3\sqrt{3}}\right)}\times 100\%$$

$$= \frac{\pi\sqrt{3}}{8}\times 100\% = 68\%$$

Inter stices or Interstitial Voids

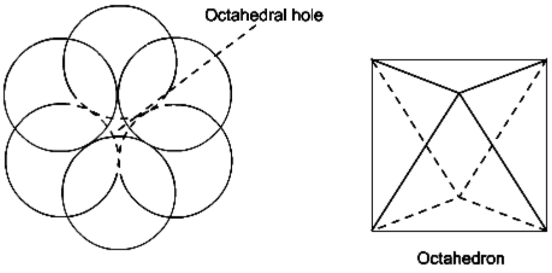
In the close packing structure, the hollows are left behind, which are called interstitial sites or interstitial voids. There are two types of voids.

(i) Tetrahedral voids.



The above arrangement of four spheres shows that their centres lie at the apices of a tetrahedron. So the vacant space among four spheres having tetrahedral arrangement is called tetrahedral void.

(ii) **Octahedral void :**



This type of void is formed at the centre of six spheres. The six spheres lie at the vertices of a regular octahedron.

Lecture - 5

Point defects : The irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance is called point defects.

Types of popint defects

(a) Stoichiometric defects

(b) Non-stoichiometric defects.

(a) Stoichiometric defects : In Stoichiometric compounds the number of +ve and –ve ions are in the same ratio indicated by their chemical formula. If any defect arises in this type of crystals the Stoichiometric of the solid is not disturbed and the defects are called stoichiometric defects.

These defects are of following types .

(i) **Schottky defect :** This type of vacancy defect is seen in ionic crystalsof the type A^+B^-, Equal number of cations and anions are missing from their lattice sites, so that electrical neutrality is maintained. This type of defect is shown by highly ionic compounds having (i) high coordination number (ii) small difference in size of cations and anions.

Examples of ionic compounds showing such defects are

NaCl, KCl, KBr, AgBr and CsCl.

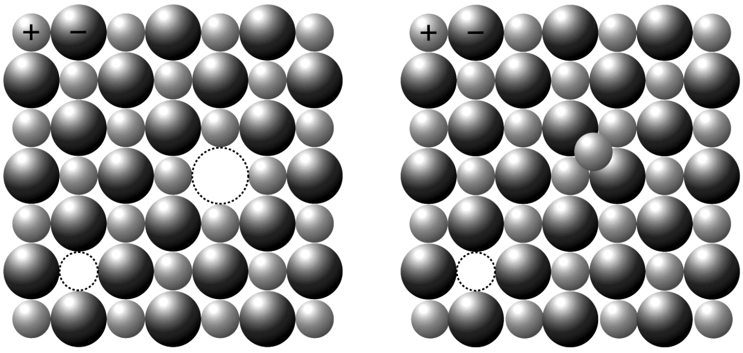
Consequences of Schottky defect

(i) As number of ions decreases, the mass decreases, where as the volume remains the same. Hence density of the solid decreases.

(ii) The number of schottkey defect increases with increase the temperature.

(iii) The lattice energy of the crystal is lowered due to presence of holes. So stability of the crystal in lowered.

(iv) The movement of atoms or ionc in the crystal is induced due to existence of a vacancies.



(a) Schottky defect **(b) Frenkel defect**

(ii) **Frenkel defect.** This type of defect is shown by ionic solids. If an ion is missing from its lattice (causing a vacancy or a hole there) and it occupies the interstitial site, electrical neutrality as well as the stoichiometry of the compounds are maintaind. This type of defect is called Frenkel defect.

This type of defect is present in compounds having

(i) Low coordination number and

(ii) Large difference in size of cations and anions.

Frenkel defect is seen in compounds like ZnS, AgCl, AgBr and AgI due to small size of Zn^{2+} and Ag^+ ions

Consequences of Frenkel defect.

(i) It has no effect on the density of the crystal.

(ii) The number of Frenkel defect increases with increase of temperature

(iii) Due to this defect the conductivity of the crystal increases

(iv) The stability of the crystal is lowered due to presence of holes in the crystal.

Defects in Non-Stoichiometric Crystals :

A large number of inorganic solids contain the constituent elements in the non-stoichiometric ratio due to defect in their crystal structure. These defects are of two types.

(a) Metal excess defect and (b) Metal deficiency defect

(a) Metal excess defect . This arises in either of the following two ways

(i) By anion vacancies :- A negative in may be missing from its lattice, leaving a hole, which is occupied by an electron, their by electrical neutrality of the crystal is maintained. The anionic sites occupied by unpaired electrons are called F-centres. (from the German word Farbenzenter for colour centre) because they are responsible for imparting colour to the crystals.

Examples : When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal, The Cl^- ions diffuse to the surface of the crystal and combine with Na^+ ions due to the loss of electrons by Na atoms. The released electrons diffuse into the crystal and occupy vacant sites created by the Cl^- ions. As a result the crystal has now an excess of sodium. KCl, LiCl also exhibit such type of defect.

(ii) By the presence of extra cations in the interstitial sites.

Metal excess is also caused when an extra cation occupies the interstitial site. Electrical conductivity is maintained by an electron present in another interstitial site.

(b) Metal deficiency defect This defect occurs when the metal shows variable valency i.e in transition metals. This defect usually occurs due to the mission of a cation from its lattice site and the presence of the cation having higher charge in the adjacent lattice site, Exa-FeO, which is mostly found with a composition of Fe 0.95^0. In crystals FeO some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+} ions.

Lecture - 6

Conduction of Electricity in metals- Metals conduct electricity and it depends upon the number of valence electrons available per atom. The atomic orbitals of metal atoms form molecular orbitals which are very close in energy and form a band. If this band is partially filled or it overlaps with a higher energy unoccupied conduction band then electrons can flow easily under an applied electric field and metal shows conductivity.

Conduction of electricity in semiconductors :

In case of semiconductors, the gap between the valence band and conduction band is small. Therefore, some electrons may jump to the conduction band show electrical conductivity. Electrical conductivity of semoconductors increases with rise in temperature, since more electrons can jump to the conduction band. substances like Si & Ge show this type os behaviour and are called intrinsic semiconductor.

The conductivity of these intrinsic semiconductors increases by adding impurity. This process is called doping. Depending upon the nature of impurity added semiconductors are of two types.

(i) **n-type semiconductor** – Silicon and germanium belong to Group 14 of the periodic table and each have four valence electrons. In their crystal each atom forms four covalent bonds with it neighbours. When doped with a Group 15 element like P or As, which contains five valence electrons, they occupy some of the lattice sites in Si or Ge crystal four out of five electrons are used in the formation of four covalent bonds with four neighbouring silicon atoms. The fifth electron is extra and becomes delocalised. These decocalised electrons increase conductivity of doped Si or Ge. Here the increase of conductivity is due to the negatively charged electron hence silicon doped with electron-rich impurity is called n-type semiconductor.

(ii) **p-type semiconductor** Si or Ge can also be doped with a Group 13 element like B, Al or Ga which contain only three valence electrons. The place where the fourth valence electron is missing is called electron hole or electron vacancy. An electron from the neighbouring atom can come and fill the electron hole but by doing so it would leave an electron hole at its original position. If it happens, it would appear as if the electron hole has moved in the direction opposite to that of the electron that filled it. Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate. This type of semiconductors are called p-type semiconductors.

Applications of n-type and p-type semiconductors.

Various combinations of n-type and p-type semiconductors are used for making electronic components (i) Diode is a combination f n-type and p-type semiconductor and is used in rectifiers.

(ii) Transistors are made by sandwitching a layer of one type of semiconductor between two layers of the other type of semiconductor. npn and pnp type of semiconductors are used to detect or amplity radio or audio signals.

(iii) The solar cell is an efficient photo-diode used for conversion of light energy into electrical energy.

Magnetic Properties :

The magnetic property of metals are due to the presence electrons. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates form its two types of motions (i) its orbital motion around the nucleus and (ii) its spin around its own axis. Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possess magnetic moment. Thus each electron has a permanent spin and an orbital. magnetic moment associated with it. Magnitude of this magnetic moment is measured in the unit called Bohr magneton. It is equal to 9.27×10^{-24} Am^2.

On the basis of their magnetic properties substances can be classified into five categories : (i) paramagnetic (ii) diamagnetic (iii) ferromagnetic (iv) antiferromagnetic and (v) ferrimagnetic

(i) **Paramegnetism :** Paramagnetism is due to presence of one or more unpaired electrons which are attracted by the magnetic field. They are weakly attracted by the magnetic field. They are magnetised in a magnetic field in the same direction and lose their magnetic field in the same direction and lose their magnetism in the absence of magnetic field.

Ex. O_2, Cu^{2+}, Fe^{3+}, Cr^{3+}.

(ii) Diamagnetism - Diamagnetism is shown by substances in which all the electrons are paired and their are no unpaired electrons. These are weakly repelled by magnetic field in opposite direction. Pairing of electrons cancel their magnetic moments and they lose their magnetic character.

(iii) Ferromagnetism : These substances are strongly attracted by magneticfield. Besides strong attractions, these substances can be permanently magnetised. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called domains. Thus each domain acts as a tiny nagnet. In an unmanaged piece of a ferromagnetic substance the domains are randomly oriented and their magnetic moments gets cancelled. When the substance is placed in the magnetic field, all the domains gas oriented in the direction of magnetic field & a strong magnetic effect is produced. The ordering domains persist even when the magneticfield is removed and the ferromagnetic substance becomes a permanent magnet.

(iv) Anti ferromagnetism : Substances which are excepted to possess paramegnetism or ferromagnetism but actually they possess zero net magnetic moment are called anti-ferromagnetic substances. In MnO, equal number of domains are oppositely oriented and cancell out each other's magnetic moment.

(v) Ferrimagnetism : Ferrimagnetism is observed when the magnetic moment of domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers. They are weakly attracted by magnetic field as compared to ferromagnetic, substances.

Example : Fe_3O_4 (magnetite), Ferrites like Mg Fe_2 O_4 and Zn Fe_2O_4. These substances on heating lose ferrimagnetism and become paromagnetic.

Lecture - 7

UNIT - II

SOLUTIONS

Solutions are homogeneous mixture of slute and solvent.

Types of solutions :-

Types Solution	Solute	Solvent	Example
Gaseous solutions	Gas	Gas	Mixture of O_2 and N_2 in air
	Liquid	Gas	Humidity in air, Chloroform mixed with N_2 gas.
	Solid	Gas	Comphor in N_2 gas, Iodine vapour in air
Liquid slutions	Gas	Liquid	O_2 dissolved in water, CO_2 dissloved in water
	Liquid	Liquid	Methanol in water
	Solid	Liquid	Salt, glu cos e, sugar solution in water
Solid slutions	Gas	Solid	Hydrogen gas adsorbed on palladium.
	Liquid	Solid	Amalgam of Hg with Na.
	Solid	Solid	Alloys-brass, German silver, bronze, 22 carat gold.

Expressing Concentration of slutions :

Percentage, grams/litre, Normality, Molarity, Molality, Mole fraction, Formality

1. (a) Percentage by mass $\left(W/_W\right)$ – It means mass of the solute in grams dissolved in 100 gms of the solvent.

Hence mass percentage = $\dfrac{\text{Mass of the solute in the solution}}{\text{Total mass of the solution}} \times 100$

(b) Percentage by volume $\left(W/_V\right)$ - It means mass of the solute in gms dissolved in 100 ml of the solvent.

Percentage $\left(W/_V\right)$ = $\dfrac{\text{Mass of the solute in the solution}}{\text{Total volume of the solution}} \times 100$

(c) Percentage by volume $\left(V/_V\right)$ – It means the volume of solute in ml dissolved in 100 ml of the solution.

Percentage $\left(V/_V\right)$ = $\dfrac{\text{Volume of solute in ml}}{\text{Total volume of solution in ml}} \times 100$

2. **Parts per million (ppm) :** It means number of parts of solute present in one million parts by mass of the solution.

$$\text{Parts per million} = \frac{\text{Number of parts of solute}}{\text{Total number of parts of all components of the solution}} \times 10^6$$

3. **Mole fraction (x) :**

Molefraction of a component = $\frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}}$.

For a solution containing n_A moles A & n_B moles of B,

$$x_A = \frac{^{n}A}{^{n}A + {}^{m}B} \text{ and } {}^{x}B = \frac{^{n}B}{^{n}A + {}^{n}B}$$

4. Molarity :-

Molarity of a solution is defined as number of gm. moles of solute dissolved in one litre of the solution.

Molarity (M) = $\frac{\text{no. of moles of solute}}{\text{volume of solution in litre}} = \frac{\text{no of gms/litre}}{\text{Molecular mass}}$

5. **Normality :** Nrmality of a solution is defined as the number of gm-equivalent mass of the solute dissolved in one litre of the solution

Normality (N) $= \frac{\text{No. of gm eq. mass of solute}}{\text{Volume of solution in litre}}$

$= \frac{\text{No. of gms/litre}}{\text{Equivalent mass}}$

6. Molality : Molality of the solution is defined as the number of moles of solute dissolved in 1000 gms of the solvent.

Molality (m) =

$$\frac{\text{Number of moles of solute}}{\text{Mass of the solvent in Kg}} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in grams}} \times 1000$$

7. Formality : It is defined as number of formula mass of the solute present per litre of the solution.

$F = \frac{W \times 1000}{M \times V}$ Where M = Formula mass of solute in gm

V = Volume of solution in ml.

W = mass of solute in gm.

In most cases formality is same as molarity.

Numericals

1. Calculate the molarity of a solution containing 5g of NaOH in 500 ml solution.

Ans. Mass of NaOH in 1 litre of solution = $(5 \times 2)\text{g} = 10\text{g}$

N. of gm moles/litre = $\frac{10}{40} = 0.25$

Hence molarity of solution = 0.25

2. Calculate the molality of 2.5g ethanoic acid (CH_3COOH) in 75 g benzene.

Mol. mass of ethanoic acid = 60 g mol^{-1}

Hence no. of moles of ethanoic acid = $\dfrac{2.5\,g}{60\,g\,mol^{-1}} = 0.0417\,mol$

Hence 0.0417 mol of ethanoic acid is present in 75 g benzene .

or, 75 g of benzene contains 0.0417 moles of ethanoic acid.

$\therefore$ 1000 g of benzene contains $\left(\dfrac{0.0415}{75} \times 1000\right)$ moles $= 0.556$ moles

$\therefore$ Molality of solution is 0.556.

3. Calculate the mole fraction of ethylene glycol ($C_2H_6O_2$) in a solution containing 20% of $C_2H_6O_2$ by mass.

Ans. Molecular mass of $C_2H_6O_2$ = 62 g mol^{-1}.

When in a solution 20% by mass of $C_2H_6O_2$ in present, it implies that the % of water is 80% by mass

$\therefore$ No. of moles of $C_2H_6O_2$ = $\dfrac{20}{62}$ = 0.332

No. of moles of water = $\dfrac{80}{18} = 4.444$

So, mole fraction of ethylene glycol = $\dfrac{0.332}{4.444 + 0.332} = 0.668.$

4. Calculate the normality of a solution obtained by mixing 10 cc of $N/2\,HCl$, 30CC of $N/10\,H_2SO_4$ and 40 cc of $N/20\,HNO_3$.

Ans. Total volume of the solution = $(10 + 30 + 40)\,cc = 80\,cc$.

10cc of $N/2\,HCl \equiv 5cc\ of\ (N)\,HCl$

$30cc\ of\ \dfrac{N}{10} H_2SO_4 \equiv$ 3 cc of (N) H_2SO_4

40 cc of $\dfrac{N}{20}$ HNO_3 $\equiv$ 2cc of (N) H_2SO_4

Let the normality of the resulting solution = x.

So 10cc of 1(N) solution = 80 cc of x(N) solution

$\therefore \quad x = \dfrac{10}{80} = 0.125$

So the normality of the solution is 0.125

Lecture - 8

Solubility : Solubility of a substance is the maximum amount of the solute that can be dissolved is a given volume of the solvent. It depends upon (i) nature of solute and solvent (ii) temperature and (iv) pressure.

Solubility of gases in liquids The solubility of any gas in a particular liquid is the volume of the gas in cc at STP that can be dissolved in unit volume (1cc) of the liquid to form a saturated solution at experimental temperature and 1 atm. pressure.

Factors affecting solubility of a gas in aliquid

(i) Nature of the gas and solvent - Easily liquifiable gases like CO_2, HCl, NH_3 etc. are highly soluble in water, but gases like H_2O_2 & N_2 dissolve to a very small extent in water.

On the other hand O_2, N_2 are more soluble in ethyl alcohol, nut H_2S and NH_3 are more soluble in water than in ethyl alcohol.

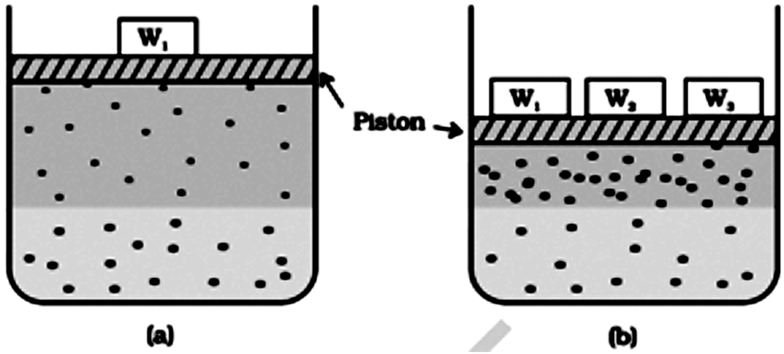
(ii) Effect of temperature – The solubility of a gas decreases with increase in temperature. The dissolution of a gas in an liquid is exothermic process.

$$\text{Gas + Solvent} \rightleftharpoons \text{Solution + Heat}$$

According to Le-chatelier's principle the increase of temperature shifts the equilibrium is the backward direction ir the slubility will decrease.

The solubility of some sparingly sluble gases such as H_2 and intergases increase slightly with increase of temperature especially in non-aqueous solvents such as hydrocarbons, alcohols and acetone.

(iii) Effect of pressure (Henry's Law)



Effect of pressure on solubility of a gas.

The solubility of a gas increases with increase of pressure for solution of gases in a slvent. Consider a system at as shown in Fig (a). The lower part is solution and the upper part is gaseous system at pressure (p) and temperature (T). Assume this system to be a state of dynamic equilibrium i.e under these conditions rate of gaseous particles entering and leaving the solution phase is the same. Now increase the pressure over the solution phase by cmpressing the gas to a smaller volume (Fig (b).

This will increase the number of gaseous particles per unit volume over the solution and also the rate at which the gaseous particles are striking the surface of the solution to enter it. The solubility of gas will increase until a near equilibrium is reached resulting in an increase in pressure of a gas above the solution and thus its solubility increases.

Henry's law gives a quantitative relation between pressure and solubility of a gas in a solvent.

Statement of Henry's law : The solubility of a gas in a liquid is directly proportional to the pressure of the gas.

or

The solubility of a gas in a liquid at a particular temperature is directly proportional to the pressure of the gas in equilibrium with the liquid at that temperature.

Mathematically : $m \propto p$ or $m = kp$

(where m = mass of the gas dissolved in unit volume of solvent

p = pressure of the gas in equilibrium with the solvent

k = proportionality constant which depends on the nature of the gas, nature of the solvent and temperature.

Expressing solubility in terms of mole fraction of the gas in the solution, for the gas 'A', Henry's law can be written as $\boxed{x_A = Kp_A}$, where x_A = mole fraction of the gas in the solution.

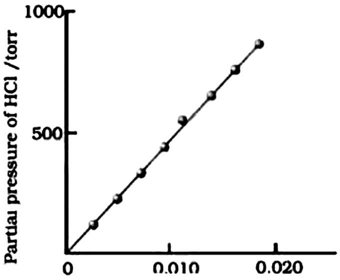
p_A = partial pressure of the gas above the solution.

$K^{/}$ = proportionality constant.

Hence Henry's law may be stated as " the mole fraction of a gas in the solution is proportional to partial pressure of the gas over the solution". or the partial pressure of the gas (p) in vapour phase is proportional to the mole fraction of the gas (x) in the solution. and is expressed as $\boxed{p = K_H \times x}$

Where K_H is Henry's constant.

The plot of partial pressure verses mole fraction given a straight line.



Mole fraction of HCl in its solution in cyclohexane

Problem

If N_2 gas is bubbled through water at 293 K, how many milli moles of N_2 gas would dissolve in 1 litre of water. Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 K bar.

Ans. The solubility of a gas is related to mole fraction in aq. solution.

$$\text{The mole fraction of Nitrogen} = \frac{\text{partial pressure } N_2}{K_H}$$

$$= \frac{0.987\,\text{bar}}{76,480} = 1.29 \times 10^{-5}$$

As one litre of water contains 55.5 mole of it, and if ‘n’ represents number of moles of N_2 in solution.

$$x_{nitrogen} = \frac{'n'\text{mole}}{'n'\text{mole} + 55.5\,\text{mol}} \approx \frac{n}{55.5} = 1.29 \times 10^{-5}$$

Hence ‘n’ = $55 \times 1.29 \times 10^{-5} = 7.16 \times 10^{-4}$ mol

= $7.16 \times 10^{-4} \times 1000$ millimole

= 0.716 millimoles

Lecture - 9

Colligative properties - The properties of ideal solutions which depend only on the number of particles of the solute (molecules or ions) dissolved in a definite amount of the solvent and and donot depend on the nature of the solute are called colligative properties. A few colligative properties are

(i) Relative lowering of vapour pressure
(ii) Elevation of boiling point
(iii) Depression in freezing point
(iv) Osmotic pressure.

(i) Relative lowering of vapour pressure : When a non-volatile solute is dissolved in a solvent, the vapour pressure of the solution is less than the vapour pressure of the pure solvent. Raoult established that the lowering of vapour pressure depends only on the concentration of the solute particles and is independent of their nature. If p^0 is the vapour pressure of pure solvent p_s is vapour pressure of the solution, then lowering of vapour pressure is $p^0 - p_s$ and relative lowering of vapour pressure is

$$\frac{p^0 - p_s}{p^0}.$$

RAOULT’S LAW : Raoult’s law states that the vapour pressure of a solution containing a non-volatile solute is proportional to mole fraction of the solvent at a given temperature.

Mathematically, $p_s \propto x_1$ (Where p_s = vapour pressure of the solution

x_1 = mole fraction of the solvent).

or, $\boxed{p_s = p^0 x_1}$ ——— (1)

Where p^0 is the vapour pressure of pure solvent.

We know that $x_1 + x_2 = 1$ (Where x_2 is the mole fraction of the solute.

Hence equation (1) can be written as

$p_s = p^0(1-x_2)$

or $\frac{p_s}{p^0} = (1 - x_2)$ or $\frac{p_s}{p^0} - 1 = -x_2$

or $1 - \frac{p_s}{p^0} = x_2$ or $\boxed{\frac{p^0 - p_s}{p^0} = x_2}$

Hence Rault’s law may be defined as “ relative lowering of vapour pressure of a solution is equal to the molefraction of the solute in the solution.

Determination of molecular mass from relative lowering of vapour pressure

We know that $\boxed{\frac{p^0 - p_s}{p^0} = x_2}$

Let ω_2 g of solute of molecular mass M_2 is dissolved in ω_1 gm of solvent of molecular mass M_1.

We know $x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1}$ (Where n_2 = no. of moles of solute

n_1 = no. of moles of solvent and n_2 <<<n_1)

$$\frac{W_2 / M_2}{W_1 / M_1}$$

$$\boxed{\frac{p^0 - p_s}{p^0} = \frac{W_2 \times M_1}{W_1 \times M_2}} \quad \text{or} \quad \boxed{M_2 = \frac{W_2 \times M_1}{W_1} \times \frac{p^0}{p^0 - p_s}} \quad \text{-------- (2)}$$

Using equation (2), molecular mass of solute can be calculated.

Problems Vapour pressure of $CHCl_3$ and CH_2Cl_2 at 298 K are 200 mm Hg and 415 mm Hg respectively. (i) Calculate the vapour pressure of the solution prepared by mixing 25.5g of $CHCl_3$ and 40g of CH_2Cl_2 at 298K (ii) mole fraction of each component in vapour phase.

Ans. Molecular mass of CH_2Cl_2 = 8.5 g mol^{-1}

Molecular mass of $CHCl_3$ = 119.5 g mol^{-1}

No of moles of CH_2Cl_2 = $\frac{40}{85} = 0.47$

No of moles of $CHCl_3$ = $\frac{25.5}{119.5} = 0.213$

Total number of moles = 0.47+0.213 = 0.683

Mole fraction of CH_2Cl_2 = $\frac{0.47}{0.683} = 0.688$

Mole fraction of $CHCl_2$ = 1–0.668 = 0.312

Total pressure of the solution = $p_{CHCl_3} + p_{CH_2Cl_2}$

$$= \left(x_{CHCl_3} \times p^0{}_{CHCl_3}\right) + \left(x_{CH_2Cl_2} \times p^0{}_{CH_2Cl_2}\right)$$

$$= \left(0.312 \times 200\right) + \left(0.688 \times 415\right) = 62.4 + 285.5 = 347.9$$

(ii) **Calculation of mole fraction of each component in vapour phase**

As calculated above $p_{CHCl_3} = 62.4\,\text{m} \,\&\, p_{CH_2Cl_2} = 285.5\,\text{ml}$.

Mole fraction of $CHCl_3$ in the vapour phax = $\frac{p_{CHCl_3}}{p_{total}} = \frac{62.4\,\text{mm}}{347.9\,\text{mm}} = 0.18$

Mole fraction CH_2Cl_2 in vapour phase = 1–0.18 = 0.82

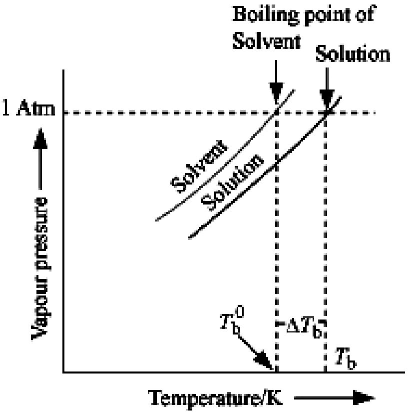
Lecture - 10

Elevation in boiling point

The boiling point of a liquid is the temperature at which the vapour pressure of the liquid becomes equal to the atmosphere pressure.

It is found that vapur pressure of the solution is less than that of the pure solvent. Hence the solution has to be heated to make the vapour pressure equal to the atmosphere pressure, because vapour pressure increases with temperature.

The elevation in boiling point may be explained by plotting vapour pressure versus temperature.



The boiling point the solvent T_b^0

The boiling point the solution = T_b

The increase in boiling point of the solution i.e., $\Delta T_b = T_b - T_b^0$ is known as elevation in boiling point.

From experiments it is found that for dilute solutions, the elevation of boiling point (ΔT_b) is directly proportional to molality of the solution

Mathematically $\Delta T_b \propto m$ or $\boxed{\Delta T_b = K_b m}$

The constant K_b is called molal elevation constant or ebullioscopic constant and m is the molality solution.

If m = 1, $\Delta T_b = K_b$, hence molal elevation constant is defined as the elevation in boiling point when the molality of the solution is unity i.e. 1 mole of the solute is dissolved in 1000 g (1 kg) of the solvent.

The unit of K_b is K kg mol^{-1}.

Determination of molecular mass of the solute

If w_2 gm of solute of molecular mass M_2 is dissolved in w_1 gm of the solvent, then

molality of the solution (m) = $\dfrac{W_2/M_2}{W_1/1000}$

Hence $\Delta T_b = K_b \times m = K_b \times \dfrac{w_2 \times 1000}{w_1 \times M_2}$ or $M_2 = \dfrac{1000 K_b \times w_2}{\Delta T_b \times w_1}$

Numericals

(1) Calculate the molal elevation constant of water, if 0.1 molal aqueous solution of a substance boiled at 100.052^{0}C.

Solution : Molality of solution = 0.1

B.P of solution = 100.052^{0}C

$$\therefore \quad \Delta T_b = K_b \times m \text{, Hence } K_b = \frac{\Delta Tb}{m} = \frac{0.052^0 C}{0.1m} = 0.52^0 C \text{ per mole.}$$

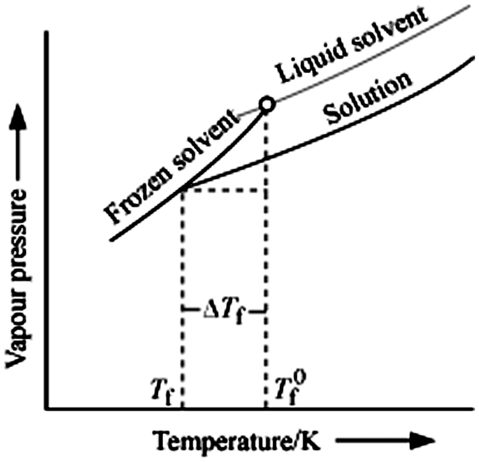
2. The b.p of benzene is 353.23 K . When 1.8 g of a non-volatile solute was dissolved in 90 g of benzene the b.p. is raised to 354.11K. Calculate the molar mass of the solute.

Ans. Given $w_2 = 1.8$ g $w_1 = 90$ g, $\Delta T_b = 354.11-353.23=0.88K$

$K_b = 2.53$ K Kg mol^{-1}

$$\therefore \quad M_2 = \frac{1000\,K_b\,W_2}{W_1 \Delta T_b} = \frac{1000 \times 2.53\,K\,Kg\,mol^{-1} \times 1.80g}{90\,g \times 0.88\,K} = 58\,g\,mol^{-1}$$

Depression in Freezing point .



The vapour pressure of a solution containing a non-volatile solute is lower than the vapour pressure of the pure solvent. Because of lowering in vapour pressure of the solution there is lowering in freezing point compared to that of the solvent. We know that at the freezing point of the substance the solid phase is in equilibrium with the liquid phase. Hence the freezing point of a substance may be defined as the temperature at which the vapour pressure of the substance in its liquid phase is equal to the vapour pressure of the pure solid phase. A solution will freeze, when its vapour pressure equals the vapour pressure of the pure solid solvent, which can be seen from Fig (1)

Let T_f^0 = the freezing point of pure solvent

T_f = The freezing point of solution containing non-volatile solute

Hence depression in freezing point = $\Delta T_f = T_f^0 - T_f$ from experiment it is known that the depression in freezing point of dilution solution (ideal solution) is directly proportional to molality of the solution.

Hence $\quad \Delta T_f = K_f \times m$

or $\quad \boxed{\Delta T_f = K_f \times m}$

Where K_f is the proportionality constant which depends on the nature of the solvent and is known as Freezing point depression constant or cryoscopic constant or Molal depression constant.

When m = 1, $\boxed{\Delta T_f = K_f}$ Hence molal depression constant may be defined as the depression in freezing point when the molality of the solution is unity i.e., 1 mole of solute is dissolved in 1000g of solvent. The unit of K_f is K kg mol^{-1}.

Calculation of Molecular mass

Let ω_2 gm of solute of molecular mass M_2 is dissolved in ω_1 gm of the solvent

Molality of solution = $\dfrac{\omega_2 / M_1}{\omega_1 / 1000}$

Hence $\Delta T_f = K_f m = K_f \times \dfrac{\omega_2 \times 1000}{\omega_1 M_2}$

or $\boxed{M_2 = \dfrac{K_f \times \omega_2 \times 1000}{\omega_1 \times \Delta T_f}}$

Problem :

1. A solution containing 34.2 g of cane-sugar ($C_{12}H_{22}O_{11}$) dissolved in 500 cm^3 of water froze at –0.374^{0}C. Calculate the freezing point depression constant of water.

Ans. Hence $\Delta T_f = -0.374\,K$

Concentration of sugar solution = 34.2 g in 500 cm^3 = 68.4g is 1000 cm^3

= 68.4 g in 1000 g water. $\left(\because d_{H_2O} = 1\,g\,cm^{-3}\right)$

$= \dfrac{68.4}{342}\,mole = 0.2\,mole$

Applying the relation $\Delta T_f = K_f \times m$, $K_f = \dfrac{\Delta T_f}{m} = \dfrac{0.374\,K}{0.2\,m} = 1.87\,K$ kg mol^{-1}

2. 1.0 g of non-electrolyte solute dissolved in 50 g benzene lowered the frezing point of benzene by 0.40 K. K_f for benzene in 5.12 K kg mol^{-1}. Calculate the molecular mass of solute.

Ans. $M_2 = \dfrac{K_f \times \omega_2 \times 1000}{\Delta T_f \times \omega_1} = \dfrac{5.12\,K\,kg\,mol^{-1} \times 1.0\,g \times 1000\,g\,Kg^{-1}}{0.40 \times 0.50\,g}$ = 256

$\therefore$ Molecular mass of solute = 256

3. 45 g ethylene glycol ($C_2H_6O_2$) is mixed with 600 g water. Calculate (a) the freezing point depression and (b) the freezing point of solution.

Ans. Molality of solution = $\dfrac{\text{no.of moles of ethylene glycol}}{\text{mass of water is kilogram}}$.

Moles of ethylene glycol = $\dfrac{45\,g}{62\,g\,mol^{-1}}$ = 0.73

Mass of water in Kg = $\dfrac{600}{1000}\dfrac{g}{Kg^{-1}} = 0.6\,Kg$

Hence molality of ethylene glycol = $\dfrac{0.73}{0.6} = 1.2$

$\therefore$ $\Delta T_f = K_f \times m$ = 1.86 K kg mol^{-1} $\times$ 1.2 mol Kg^{-1} = 2.2 K

$\therefore$ Freezing point of aqueous = $(273.15 - 2.2)\,K$

= 270. 95 K

Lecture - 11 & 12

OSMOSIS

Osmosis - The spontaneous flow of the solvent into solution through a semipermeable membrane or flow of solvent from more dilute solution to a concentrated solution through the semipermiable membrane is called osmosis.

Osmotic pressure. The excess pressure that must be applied on the solution to check the inflow of the solvent into it is called osmotic pressure.

Isotonic solution - Solutions having some osmotioc pressure are called isotonic solutions.

Hypertonic and hypotonic solution - The osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/volume). If we place a blood cell in a solution containing more than 0.9% (mass/volume) sodium chloride, water will flow out of the cell and the cell would shrink. Such a solution is called hypertonic solution.

On the other hand if the concentration of sodium chloride is less than 0.9% (m/v), the solution is said to be hypotonic. In this case, water will flow into the cells if placed in this solution and they will swell.

Determination of Molecular mass from osmotic pressure measurement

Osmotic pressure is proportional to the molarity (C) of the solution at a given temperature(T).

Mathematically $\pi = CRT$ ———— (1)

Where π = osmotic pressure and R is the gas of constant. If n_2 moles of solute is present in V litres of solution, then $C = {}^{n_2}\!/_{V}$

Hence eq^n (1) becomes $\pi = \frac{n_2}{C} RT$ —— (2)

If w_2 g of solute of molecular mass M_2 is present in the slution, then $n_2 = {}^{W_2}\!/_{M_2}$, so equation (2) can be written by

$$\pi = \frac{W_2 RT}{V M_2} \quad \text{or} \quad \boxed{M_2 = \frac{W_2 RT}{\pi V}} \text{ —— (3),}$$

Henc knowing W_2, T, π and V molecular mass os solute can be determined from equation (3).

Problem :

1. 200 cm^3 of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressusre of such a solution at 300 K is found to be 2.57×10^{-3} bar. Calculate the molecular mass of the protein.

Ans. $\pi = 2.57 \times 10^{-3}$ bar mol^{-1} K^{-1}

R = 0.082 L bar mol^{-1} K^{-1}

$$\therefore \quad M_2 = \frac{W_2 RT}{\pi V} = \frac{1.26\,g \times 0.082\,L\,bar\,K^{+}\,mol^{-1} \times 300\,K}{2.57 \times 10^{-3}\,bar \times 0.2\,L}$$

$$\boxed{M_2 = 61{,}022}$$

2. Calculate the osmotic pressure in pascals exerted by a solution prepared by dissloving 1.0 g of polymer of molecular mass 185, 000 in 450 ml of water at 37^{0}C.

Ans. T = 273+37 = 310 K, M = 185, 000, V = 450ml = 0.45 litre

$$\therefore \quad \pi = \frac{W_2RT}{M_2V} = \frac{1.0\,g \times 0.082\,litre\,atom\,\partial ef^{-1}\,mol^{-1} \times 310}{1,85,000 \times 0.45\,L}$$

$$=$$

3. Calculate the osmotic pressure at 273 K of a 5% solution of urea.
(R = 0.082 litre atm/degree/mole).

Ans. $$\pi = \frac{W_2RT}{M_2V} = \frac{5g \times 0.082\,litre\,atm\,K^{-1}\,mol^{-1} \times 273\,K}{\left(60\,g\,mol^{-1}\right)\left(0.1L\right)} = 18.68\,atm.$$

$$\left(V = 100\,cm^3 = 0.1\,litre\right)$$

4. A 4% solution of sucrose $C_{12}H_{22}O_{11}$ is isotonic with 3% solution of an unknown organic substance. Calculate the molar mass of the unknown substance.

Ans. Since the two solutions are isotonic, they must have same concentration in moles/ litre.

For sucrose solution we have, concentration = 4g/100 cm^3 = 40g/litre

$$= \frac{40}{342}\,moles\,/\,litre$$

For unknown substance, suppose 'M' is the molecular mass, then

$$\text{concentration} = 3g/100\,cm^3 = 30g\,/\,litre = \frac{30}{M}\,moles\,/\,litre$$

$$\text{Hence } \frac{30}{M} = \frac{40}{342}, \text{ or } M = \frac{342 \times 30}{40} = 265.5\,g\,mol^{-1}$$

Lecture - 13

Abnormal Colligative properties :

The colligative properties of solutions depends on the number of solute particle present in the solution. If the total number of particles of the solute in the solution changes, the colligative property will change accordingly. A solution containing one mole of electrolyte like NaCl will contain 2 moles of particles (1 mole of Na^+ and 1 mole of Cl^{-1} ions). Similarly 1 mole of $BaCl_2$ will contain 3 miles of ions in the solution. When benzoic acid is dissolved in benzene, benzene acid molecules dimerse for which number of particles becomes half.

Since the molecular mass is inversely proportional to colligative properties, in case of dissociation of solute, the observed molecular mass will be less than the calculated value and incase of association, the observed molecular mass will be more than the calculated value. such a molecular mass that is either higher or lower than the normal or calculated value is called as abnormal molecular mass.

In 1880, van't Hoff introduced a factor 'i' known as the van't Hoff factor, to account for the extent of dissociation or association. This factor 'i' is defined as, the ratio of the experimental value of colligative property to the calculated value of the colligative property.

$$\text{So } i = \frac{\text{Experimental value of colligative property}}{\text{Calculated value of colligative property when the solute behaves ideally.}}$$

$$= \frac{\text{Obser value value of colligative property}}{\text{Calculated or normal value of colligative property}}$$

Further, as the colligative mass is the experimentally determined molecular mass and calculated molecular mass as obtained by assuming, that non-volatile solute is neither associated or dissociated. In case of association 'i' is less than unity, but in case of dissociaton it is greater than units.

Application of Van't Hoff factor :

Using van't Hoff factors the degree of dissociation and association can be calculated as follows :

(i) Calculation of degree of dissociation

Degree of association is defined as the fraction of total substance that undergoes dissociation

$$\text{i.e., Degree dissociation} = \frac{\text{No. of moles dissociated}}{\text{Total number of moles taken}}$$

Suppose one molecule of the solute dissociated to give 'n' ions and 'α' is the degree of dissociation.

$$A \longrightarrow n_1 B + n_2 C + \text{..........} \quad (\text{Where } n_1 + n_2 + \text{....} = n)$$

If we start with 1 mole of slute, at equilibrium we have $(1-\alpha)$ moles of undissociated molecules and $n\alpha$ moles of ions.

So tatl no. of moles of ions and the undissociated

molecules = $1-\alpha+n\alpha = 1+(n-1)\alpha$

Hence the observed colligative property $\alpha\ 1+(n-1)\alpha$.

Normal (or thearetical) value of colligative property α 1 (as one mole of A' is takes)

$$\therefore \quad \text{Van't Hoff factor} = i = \frac{1+(n-1)\alpha}{1}$$

$$\text{or} \quad \alpha = \frac{i-1}{n-1} \qquad \_\_\_\_\_\_\_\_\_\_(1)$$

$$\text{But } i = \frac{\text{Calculated molecular mass}}{\text{observed molecular mass}} = \frac{M_C}{M_0}$$

$$\therefore \quad \alpha = \frac{{}^{M_C}\!/\!_{M_0} - 1}{n-1} = \frac{M_C - M_0}{N_0(n-1)} \qquad \_\_\_\_\_\_\_\_\_\_(2)$$

From equation (1) & (2) , the degree of dissociation (α) of the solute can be calculated.

ii) Degree association : It is defined as the fraction of the total substance which exist in the form of associated molecules.

$$\therefore \quad \text{Degree association } (\alpha) = \frac{\text{No of moles associated}}{\text{Total number of moles taken}}$$

Suppose ‘n’ simple molecules of solute ‘A’ associate to form the associated molecule An, & that we have the equilibrium

$$nA \rightleftharpoons An$$

If α is the degree of association and we start with one mole of A, then at equilibrium.

Normal f moles of A = $1-\alpha$

Number of moles of $A_n = \frac{\alpha}{n}$

$$\therefore \quad \text{Total number of moles} = 1-\alpha+\frac{\alpha}{n}$$

Since colligative property is proportional to the number of moles of the solute present in the solution.

$$i = \frac{1-\alpha+\alpha/n}{1} \quad \text{or} \quad \alpha = (1-i)\frac{n}{n-1} \text{ ________ (1)}$$

We know colligative property $\alpha \frac{1}{\text{molecular mass}}$

$$1-\alpha+\frac{\alpha}{n} = \frac{M_C}{M_0}$$

(Where M_C = calculated normal molecular mass.)

(M_0 = observed molecular mass

$$\text{or} \quad 1-\frac{M_C}{M_0} = \alpha-\frac{\alpha}{n}$$

$$\text{or} \quad 1-\frac{M_0-M_C}{M_0} = \alpha\left(1-1/n\right) = \alpha\left(\frac{n-1}{n}\right)$$

$$\therefore \quad \alpha = \frac{M_0-M_C}{M_0}\times\frac{n}{n-1} \text{ ____________ (2)}$$

From equation (1) & (2) the degree of association (α) can be calculated.

AZEOTROPES

In case of solutions showing positive deviations from Raoult’s lar, at one of the intermediate compositions the total vapour of the highest and the boiling point is the lowest. In case of solutions showing negative deviations from Raoult’slar for one intermediate composition, the vapour pressure is the lowest and the boiling point is the highest. For liquid pairs of such intermediate composition, the composition of the liquid and vapour phase is the same. So when liquid mixture of such a composition vaporises without change in composition, the liquid obtained by the condensation of the vapour, also has same composition. The composition of such a mixture in of course fixed.

This type of liquid mixture, having a definite composition and boiling like a pure liquid is called a constant boiling mixture a zeotropic mixture or an azeotrope.

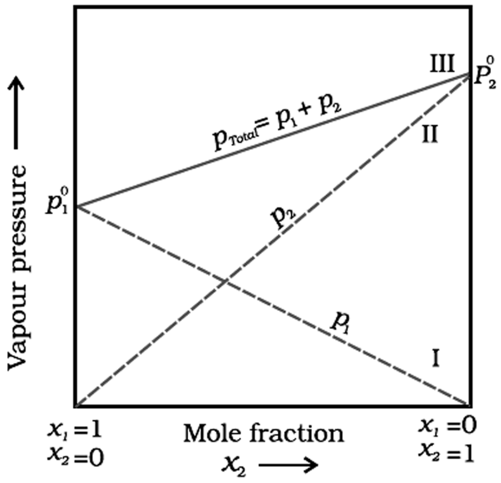
Lecture - 14

Ideal solution : In an ideal solution each component obeys Roult's law under all conditions of temperature and pressure. The ideal solution should satisft the following conditions.

(i) There will be no change of colume on mixing the two components i.e., $\Delta V_{mixing} = 0$

(ii) There will be no change in enthalpy when the two components are mixed i.e., $\Delta H_{mixing} = 0$

(iii) Solute – solvent interaction = solvent - solventintraction = soulte -solute interaction



Examples :

(i) Ethyl chloride + Ethyl bromide

(ii) Benzene + Toluene

(iii) Chloro benzene + Bromo benzene

(iv) n-heaane + n-heptane

According to Raoult's law, a plot of P_A or P_B against x_A and x_B for a solution should give a straight line. I and II ; passing through the points P_A^0 and P_B^0 when x_A and x_B equals to units. The total vapour pressure P exerted by the solution as a whole at any composition is given by $P_A + P_B$m indicated by line III.

a) Non-ideal solution : The solution which does not obey Raoult's law is called non-ideal solution.

For such solutions $\Delta V_{mixing} \neq 0$, $\Delta H_{mixing} \neq 0$ for example when we mix H_2SO_4 in water, the amount of heat generated is large and change in volume is also observed.

(i) Non-ideal solution exhibiting positive deviations

When a component B is added to another component A, some times the partial pressure of a component A is found to be more than expected on the basis of Raoult's law.

The total vapour pressure for any solution is thus greater than that corresponding to an ideal solution of same composition.

Such behaviour of solutions is described as a positive deviation from Raoult's law.

The boiling point of such solutions are relatrively lower as compared to those of pure components (because higher the vapour pressure, lower is the boiling point). For one intermediate composition, the total vapoue pressusre of such a solution will be the highest and the boiling point will be the lowest. This solution acqures the property of boiling at a constant temperature and its composition remains unchanged. Liquid mixtures which distil without any change in composition are called azeotropes or a zeotropic mixtures. In case of solutions showing positive deviations. We get minimum boiling point azeotropes.

(i) Acetone + carbon di sulphide
(ii) Acetone + benzene
(iii) Ethyl alcohol + water
(iv) Acetone + Ethylalcohol
(v) Carbon tetra chloride + Chloroform.

(ii) Non-ideal solutions showing negative deviation.

If is a solution for the two components A and B, the forcs of interaction between A and B molecules are more than the A–A and B–B forces of interaction, the total vapour pressure of the solution is less than that corresponding to an ideal solution obeying Raoult's law of the same composition, at the same temperature. These solutions are said to show negative deviations from Raoult's law. Such solutions have relatively higher boiling points as compared to those of the pure components. For one intermediate composition, the total vapour pressure of the solution will be the least and the boiling point will be the highest. such a solution will also distil without any change in composition and provides an example of another kind of ozeotrope known as maximum boiling point azeotrope.

Examples of non-ideal solutions showing negative deviations :

(i) Chloro form + acetone
(ii) Acetic acid + pyridine
(iii) Water + Nitric acid
(iv) Chloroform + benzene
(v) HCl + water

Lecture - 15 and 16

UNIT - III

Electro Chemistry

Electrolytes - The substances which conduct electricity in fused state or in aqueous solutions are called electrolytes.

Examples- acids bases, salts of acids and bases

Non-electrolytes- The substances which donot conduct electricity in their aqueous solutions are called non-electrolytes.

Example - Sugar, Urea, benzene.

Metallic or Electronic conductors - The metals through which electric current can pass due to the migration of electrons are called metallic or electronic conductors.

Degree of dissociation– The fraction of total number of molecules dissociated is called degree of dissociation.

$$\text{Degree of dissociation} = \frac{\text{Number of molecules dissociated into ions}}{\text{Total number of molecules dissolved}}$$ on the basis of

degree of dissociation electrolytes – Electrolytes which are almost dissociated or having high degree of dissociation are called strong electrolytes.

1) Strong electrolytes – electrolytes which are almost dissociated or having high degree of dissociation are called strong electrolytes.

Example. Strong acids (HCl, H_2SO_4, HNO_3 etc) strong bases (NaOH, KOH), salts of strong acids and strong bases (NaCl, KCl, KNO_3, Na_2SO_4) and OHeX salts.

2) Weak electrolytes - The electrolytes which are dissociated to a small extent are called weak electrolytes.

Example - Weak acids (CH_3COOH, HCOOH etc), bases like NH_4OH.

Electrolysis : The process of decomposition of an electrolyte in solution or in fused satte by passing electric current is called electrolysis.

An aqueous solution of an electrolyte is taken in a glass vessel. Tow metal plates called electrodes are dipped in it and are connected to the positive and negative pole of the battery. The electrode connected to the positive pole is called anode and that connected to the negative pole is called cathods. Electric current enters the electrolyte through the anode and leaves the electrolyte through the cathode.

By passing current the positive ions or cations move towards the cathode and are discharged there, the negative ions are discharged at the anode.

Example

(1) Electrolysis of fused NaCl

$$\mathrm{NaCl} \longrightarrow \mathrm{Na}^+ + \mathrm{Cl}^-$$

At cathode $\mathrm{Na}^+ + e \longrightarrow \mathrm{Na(metal)}$ (reduction)

At anode $2\mathrm{Cl}^- \longrightarrow 2e + \mathrm{Cl}_2$ (oxidation)

(2) Electrolysis of aqueous NaCl solution

$$\mathrm{NaCl} \longrightarrow \mathrm{Na}^+ + \mathrm{Cl}^-$$

At cathode $H^+ + e^- \longrightarrow \frac{1}{2}H_2$

$$\frac{H_2O \longrightarrow H^+ + OH}{H_2O + 2e^- \longrightarrow \frac{1}{2}H_2 + OH^-}$$

At anode- $2Cl^- \to 2e + Cl_2$.

Faraday's Laws of Electrolysis.

1) Faraday's first law - The mass of the substance discharged (deposited or liberated) at the cathode is directly proportional to the quantity of electricity passing through the electrolytic solution.

Mathematically $w \propto \theta$ ——(1) (Where w = mass of the substance in gms

θ = quantity of electricity in columnbs)

But we know $\theta = c \times t$ (c = current strength in amperes

t = time in second.

Hence equation (1) can be written as

$w \propto c \times t$

or $\boxed{W = z \times c \times t}$ Where 'Z' is a proportionality constant called electrochemical equivalent of the substance.

When c = 1 ampere

t = 1 second

$w = x \times 1 \times 1$ or W= Z

Hence electron chemical equivalent (ECE) of a substance can defined as the mass of the substance deposited or liberated by passing one ampere of current for one second. (i.e. on passage one coulomb of electricity)

Ques. (1) Calculate ECE of silver.

Ans. 96500 Coulombs (i.e., 1 Faraday) of electricity deposits 108 g of silver.

Hence 1 coulomb of electricity will deposet $\frac{108}{96500} = 0.001118\,\text{gm}$ of silver

$\therefore$ ECE of silver = 0.001118'

(2) What is ECE of copper ?

Ans. $\frac{31.75\,g}{96500 \text{ Coulomb}} = 0.000329$ gram/coulomb

Faraday's 2nd Law of electrolysis. When the same quantity of electricity is passed through different electrolytes connected in series, the amount of different substances deposited or liberated at the electrodes are proportional to their chemical equivalents i.e., equivalent masses.

Explanation Let us consider three cells containing acidulated water, $CuSO_4$ solution and $AgNO_3$ solution are connected in series and same quantity of electricity say one Faraday is passed through these solution. It will be seen that 1 g equivalent mass of hydrogen i.e., (1.008 g) one gm equivalent mass of silver (i.e., 108 gm) will be liberated.

Suppose due to passage of same quantity of electricity w_1, w_2 and w_2 gm of elements are liberated whose equivalent masses are E_1, E_2 and E_3 respectively.

According to Faraday's second law

$$\frac{W_1}{W_2}=\frac{E_1}{F_2}\text{and}\frac{W_2}{W_3}=\frac{E_2}{E_3}$$

If z_1, z_2 and z_3 are the electrochemical equivalents of the elements, then according to Faraday's first law silve W=ZCt, and quantity of electricity (c.t) is constant we can write

$$\boxed{\frac{W_1}{W_2}=\frac{E_1}{E_2}-\frac{Z_1}{Z_2}} \text{ and } \boxed{\frac{W_2}{W_2}=\frac{E_2}{E_3}-\frac{Z_2}{Z_3}}$$

Problems :

1. A current of 3 amper is passed through $AgNO_3$ solution for 20 minutes and 4 gram silver is deposited. Calculate ECE of silver.

Ans. We know W = zct

Hence $z=\frac{W}{c\times t}=\frac{4}{3\times 20\times 60}=0.00111$

2. 0.30 g copper was deposited on passage of 5 amp. of current for 30 minutes through copper sulphate solution. Calculate atomic mass of copper.

Ans. $Q=(5\times 30\times 60)=900\,\text{coulmbs}$

$C_u^{2+}+2e\rightarrow Cu$

900 coulombs of electricity deposits 0.3g copper

Hence 1 coulombs of electricity will deposit $\frac{0.3}{900}g$ of copper.

$\therefore$ ECE of copper $=\frac{0.3}{900}$

Equivalent mass of copper = ECE $\times$ 96500 $\Rightarrow E = Z.F$

$=\frac{0.3}{900}\times 96500=32.166$

We know atomic mass = Equivalent mass $\times$ valency

$\therefore$ Atomic mass of copper = $32.166\times 2=64.333.$

3. Calculate ECE of Cu and Ag, when ECE of hydrogen is 0.0000104

Ans. $$\frac{\text{ECE of } H_2}{\text{ECE of Ag}}=\frac{\text{Equivalent mass of hydrogen}}{\text{Equivalent mass of silver}}$$

or $$\frac{0.0000104}{Z_{Ag}}=\frac{1.008}{108}$$

$\therefore$ $$Z_{Ag}=\frac{108\times 0.0000104}{1.008}=0.00111\text{ gm/C}$$

Similarly $$Z_{cu}=\frac{31.75\times 0.0000104}{1.008}=0.0003275$$

Lecture- 17 and 18

Electrolytic conductance - The Ohm's law valid for metallic conductors is also applicable to electrolytic conductors.

Ohm's law : The strength of the current(I) passing through a conductor is (i) directly proportional to the potential difference (E) applied across the conductors and (ii) inversely proportional to the resistance (R) of the conductor.

Hence $\boxed{I = \frac{E}{R}}$ where I is an amperes, E is volts and R is in ohms

Resistance(R) The resistance of any conductor is directly proportional to the length f the cnductor (l) and inversely proportional to the area of cross section of the conductor(a)

Hence $R \propto \ell$ .... (1)

$R \propto \frac{1}{a}$ ....(2)

Combing equation (1) & (2), we get $R \propto \frac{\ell}{a}$

or $R = \rho \frac{\ell}{\sigma}$, where ρ(rho) is a constant and is called specific resistance.

When $\ell = 1\text{cm}$, a = 1 cm^2,

$\boxed{R = \rho}$, Hence specific conductance is equal to resistance in ohms of a material of length 1cm and area of cross section 1 cm^2. Unit of resistance is Ohm.

Conductance (C) : It is reciprocal of resistance and having unit ohm^{-1} or mho

we know $R = \rho \frac{l}{a}$

or $R = \frac{1}{k} \frac{\ell}{a}$ or $\boxed{k = \frac{1}{R} \times \frac{\ell}{a}}$ = Conductance cell const.

($\therefore$ $1/a$ = cell constant)

So unit of specific conductance is ohm^{-1} cm^{-1} or mho cm^{-1}.

(G*) Cell constant $\left(\ell/a\right) = K \times R$ = Specific conductance × resistance

$$G^* = \frac{\text{specific conductance}}{\text{conductance}}$$

specific conductance – It is defined as conducting power of all ions present in a cell in which the electrodes are 1 cm apart and have cross-sectional area of 1 cm^2.

or

Specific conductance is defined as the conducting power of all ions present in 1 cm^3 of an electrolytic solution.

Equivalent conductance ($\wedge$) $\therefore$ It is defined as the conducting power of all ions produced by one gm equivalent of an electrolyte in a given volume of the solution.

It is related to specific conductance as

$\wedge = \frac{1000\,k}{C}$, Where k = specific conductance

C = concentration of the slolution in gm equivalent peritre or normality

or $\wedge = kV$ (Where V is the volume of solution containing 1gm eq of electrolyte)

Units of $\wedge$ = $ohm^{-1}\ cm^{2}$ gm $equivalent^{-1}$.

Molar conductance (μ) : It is defined the conducting power of all ions produced by one gm mole of an electrolyte in a given volume of the solution.

$$\mu = \frac{1000\,k}{m}$$ (Where m = molarity of the solution

$$= k \times V$$ (V = volume of solution containing one gm mole of solute)

Variation of conductivity with dilution

Strong electrolytes are almost ionized in an aqueous solution. With dilution the force of attraction between positive and negative a ions decreases. On the otherhand in case of weak electrolytes the degree of ionisation increases with dilution, hence no doubt the number of ions in the solution go on increasiung, but number of ions per cubic centrimeter go on decreasing. As a result specific conductance decreases with dilution and molar conductance increases with dilution.

Problems :

1. A decinormal solution of sodium acetate when placed between two electrodes each 1.5 cm square of cross section and placed at a distance of 0.72 cm has a resistance of 52.4 ohm. Calculate specific conductance and equivalent conductance

Ans. $R = \rho\frac{\ell}{a}$, 52.4 = $\rho \times \frac{0.72}{1.5}$ or $\rho = \frac{52.4 \times 1.5}{0.72}$ = 163.8 ohm. cm.

$$\therefore \quad k = \text{Specific conductance} = \frac{1}{\rho} = \frac{1}{163.8} = 0.0061\ ohm^{-1}\ cm^{-1}$$

$$\wedge = \frac{1000\,k}{C} = \frac{1000 \times 0.0061}{0.1} = 61 ohm^{-1}\ cm^{2}\ g\ equiv^{-1}.$$

2. Specific conductance of 0.2 mol $litre^{-1}$ solution of KCl is 2.48×10^{-2} ohm cm^{-1}. Calculate molar conductance.

Ans. $\mu = \frac{1000\,K}{m} = \frac{1000 \times 2.48 \times 10^{-2}}{0.2} = 124\ ohm^{-1}\ cm^{2}\ gmol^{-1}$

3. If specific conductivity of $^{N}\!/_{50}$ KCl solution at 298 K is 0.002765 $ohm^{-1}cm^{-1}$ and resistance of the cell containing the solution is 100 ohms, Calculate the cell constant

Ans. Cell constance = specific conductance $\times$ resistance

$$= (0.002765 \times 100) = 0.2765\,cm^{-1}.$$

4. The resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 ohm. If the resistance of the same cell filled with 0.02 mol L^{-1} KCl solution is 520 ohm, Calculate the conductivity of 0.02 M KCl solution. The conductivity of 0.1 M KCl solution is 1.29 S/m.

Ans. For 0.1M KCl solution, R = 100 ohm, K = 1.29 Sm^{-1}

Cell constant = Conductivity × resistance

$= 1.29\ Sm^{-1} \times 100\ ohm = 129\ m^{-1} = 1.29\ cm^{-1}$

(ii) Conductivity of 0.02 M KCl solution = (K) = $\dfrac{\text{Cell constant}}{\text{Resistance}}$

$$= \frac{129\,m^{-1}}{520\,ohm} = 0.248\,ohm^{-1}\,m^{-1}$$

Concentration of the solution = 0.02 M

$\therefore$ Molar conductivity = $\dfrac{1000k}{C} = \dfrac{1000 \times 0.00248\,ohm^{-1}\,cm^{-1}}{0.02}$

$= 124\ ohm^{-1}\ cm^2\ mol^{-1}$

Kohlrausch Law :

Statement - At infinite dilution when dissociation of an electrolyte is complete, each ion makes a definite contribution towards the equivalent conductance of the electrolyte irrespective of the nature of the other ion with which it is associated and the value of equivalent conductance of any electrolyte at infinite dilution is given by the sum of ionic conductances of the constituent ions.

Explanation : If λ^0_+ and λ^0_- represent the ionic conductances of all the positive and negative ions respectively at infinite dilution, then equivalent conductance of the electrolyte at inifinite dilution $\left(\Lambda^0\right)$ is given by

$$\boxed{\Lambda^0 = \lambda^0_+ + \lambda^0_-}$$

Example : $\Lambda^0{}_{NaCl} = \lambda_{Na^+} + \lambda^0_{Cl^-}$

Application (1) Calculate of equivalent conductance of acetic acid at infinite dilution.

$$\Lambda^0{}_{CH_3COOH} = \lambda^0{}_{CH_3COO^-} + \lambda^0_{H^+}$$

$$\Lambda^0{}_{CH_3COONa} + \lambda^0{}_{HCl} - \Lambda^0{}_{NaCl} = \left(\lambda^0{}_{CH_3COO^-} + \lambda^0 Na^+\right) + \left(\lambda^0_{H^+} + \lambda^0_{Cl^-}\right) - \left(\lambda^0_{Na^+} + \lambda^0_{Cl^-}\right)$$

$$= \lambda^0_{CH_3COO^-} + \lambda^0_{H^+}$$

$$= \Lambda^0_{CH_3COOH}$$

Hence knowing the equivalent cnductances of CH_3COONa, NaCl and HCl at infinite dilution that of $\Lambda^0_{CH_3COOH}$ can be calculated

2. **Calculation of** $\Lambda^0_{NH_4OH}$

$$\Lambda^0 NH_4OH = \lambda^0 NH_4^+ + \lambda^0_{OH} -$$

$$\Lambda^0 NH_4Cl + = \Lambda^0 NaOH - \Lambda^0 NaCl = \lambda^0 NH_4^+ + \lambda^0_{Cl^-} + \lambda^0_{Na^+} + \lambda^0 OH^-$$

$$-\ \lambda^0 Na^+ - \lambda^0 Cl^- = \lambda^0 NH_4{}^+ + \lambda^0 OH^- = \Lambda^0 NH_4OH$$

Hence knowing the equivalent conductance at infinite dilution of NH_4Cl, NaOH & NaCl, $\Lambda^0 NH_4OH$ can be calculated.

Problems :

1. Equivalent conductance at infinite dilution of NH_4Cl, NaOH and NaCl are 129.8, 217.4 and 10845 $ohm^{-1}cm^2$ g eq^{-1} respectively. Determine the equivalent conductance of NH_4OH.

Ans. $\Lambda^0 NH_4OH = \Lambda^0 NH_4Cl + \Lambda^0 NaOH - \Lambda^0 NaCl$

$$= 129.8 + 217.4 - 108.45$$

$$= 238.74\,\text{ohm}^{-1}\,\text{cm}^2\ \text{gm equivalent}^{-1}$$

2. Equivalent conductance of sodium propionate, HCl and NaCl at infinite dilution are 85.9, 426.1 and 126.4 mho cm^2 eq^{-1} respectively at 298K. Calculate equivalent conductance at infinite dilution for propionic acid.

Ans. $\Lambda^0 CH_3CH_2COOH = \Lambda^0 CH_3CH_2COONa + \Lambda^0 HCl - \Lambda^0 NaCl$

$$= (85.9 + 426.1 - 126.4)\ \text{ohm}^{-1}\ \text{cm}^2\text{gm eq}^{-1}$$

$$= 385.6\ \text{ohm}^{-1}\ \text{cm}^2\ \text{gm eq}^{-1}.$$

Lecture-19

(i) **Eletrolytic cell :** It is a device in which electrical energy is converted to chemical energy.

(ii) **Electro chemical cells :** It is a device in which chemical energy produced due to redox reaction is converted to electrical energy. A voltic cellor Galfanic cell is an example of an electrochemical cell. In one beaker a zinc rod is dipped in $ZnSO_4$ $(aq)^v$ in another beaker a copper rod is dipped in $CuSO_4$ olutions. Both zinc rod and copper rod are connected to the voltmeter. A salt bridge is used to make electrical contact between the two solutions. Here zinc rod serves as the anode and the copper rod series as the cathode. Here because of redox reaction electrical energy is produced.

Reactions in the Galvonic cell.

$$\begin{array}{lll} \text{At anode} & Zn(s) \longrightarrow Zn^{2+}(aq) + Ze & \text{(oxidation)} \\ \text{At cathode} & Cu^{2+}(aq) + 2e \longrightarrow Cu(s) & \text{(reduction)} \\ \hline \text{Overal cell reaction :} & Zn(s) + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}(aq) + Cu(s) & \end{array}$$

Daniel cell : The galvanic cell in which $CuSO_4$ and $ZnSO_4$ solutions are taken in the same bearer and they are separated by a porous diaphragm, it is called Daniell cell. If the concentration of both $CuSO_4$ and $ZnSO_4$ are 1(M), then emf produced in this cell is 1.10 volt at 25^0 C.

The Galvonic cell is represented as

$$Zn(s)\,|\,ZnSO_4(aq)\ ||\,CuSO_4(aq)\ |\,Cu(s)$$

$$Zn(s)\,|\,Zn^{2+}(aq)\ ||\,Cu^{2+}(aq)\ |\,Cu$$

The Daniel cell is represented as

$$Zn(s)\,\Big|\,Zn^{2+}(aq)\ \vdots\,Cu^{2+}(aq)\ \Big|\,Cu$$

It is a primary battery (cell).

Drycell : It is a primary battery. λ These are used in transistors and clocks and these are compact form of the Leclanch cell. The dry cell is a voltaic or galvanic cell used for production of electricity. In the dry cells the reaction occurs only once and after use over a period of time battery becomes dead and can not be used again. The cell consists of a Zinc container that acts as the anode and graphite rods placed in the centre acts as the cathode. The space between the anode and cathode is packed with paste of NH_4Cl and $ZnCl_2$ and graphite rod is sorrounded by powdered MnO_2 and carbon. The graphite rod is fitted with a metal cap and the cylinder is sealed at the top with pitch. The zinc container is covered with card board to protect it from atmosphere.

The eelctrode reactions are complex, but they can be written in simple manner as :

At anode : $\mathrm{Zn(s)} \longrightarrow \mathrm{Zn^{2+} + (aq) + 2e}$

At cathode : $\mathrm{2MnO_2 + 2NH_4^+ + 2e \longrightarrow Mn_2O_3(s) + 2NH_3(g) + H_2O}$

At the cathode Mn is reduced from +4 oxidation state to +3 oxidation state. Ammonia produced in the reaction forms a complex with Zn^{2+} ion to form $\left[\mathrm{Zn(NH_3)_4}\right]\mathrm{Cl_2}$.

The cell potential is nearly 1.5 V.

Lead accumulator (Lead storage battery)

It is a secondary cell, which after use can be recharged by passing current through it in the opposite direction, so that it can be used again. These are used in automobils and invertors. A 12V lead storage battery is generally used which consists of 6 cells each producing 2V. Each cell consists of a lead anode and a grid of lead packed with lead oxide (PbO_2) as cathode. A 38% solution of H_2SO_4 is used as an electrolyte. The cell reaction when the battery is used (i.e., discharging process) is given below. The electrode reaction that occurs during discharge (i.e. when the battery is in use) are as follows

At anode : $\mathrm{Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e(Oxidation)}$

At cathode :

$$\mathrm{PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e \rightarrow PbSO_4(s) + 2H_2O(reduction)}$$

Overall reaction : $\mathrm{Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \rightarrow 2PbSO_4(s) + 2H_2O}$

From the reaction it is obvious that H_2SO_4 is used up during the discharge. As a result the density of H_2SO_4 falls and when it falls below 1.20g cm^{-3}, the battery needs recharging.

During recharging the cell operates like an electrolytic cell i.e., electrical energy is supplied to it from external source. The electrode reactions are the reverse of those that occur during discharge.

At cathode : $\mathrm{PbSO_4(s) + 2e \rightarrow Pb(s) + SO_4^{2-}(aq)\,Reduction}$

At anode : $\mathrm{PbSO_4(s) + 2H_2O \rightarrow PbO_2(s) + SO_4^{2-}(aq) + 2e(oxidation)}$

Overal reaction : $\mathrm{2PbSO_4(s) + 2H_2O \rightarrow Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq)}$

LECTURE - 20 to 24

EMF of a cell : (E) The difference between the electrode potential of two half cell is known as cell potential and is measured in volts. It is called the electromotive force (emf) of the cell when no current is drawn from the cell.

When concentration all the species involved in each half-cell is unity, then the emf of the cell is called standard emf (E^0)

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

(where $E^0_{cathode}$ = standard reduction potential of cathode and E^0_{anode} = standard reduction potential of anode).

Electrochemical Series

Arrangement of elements in the increasing order of their reduction potentials is called electrochemical series. Cateulated ert. S HE taken as zero volt. Standard reduction potential of a few metals is given below.

	Standard reduction potential $\left(E^0_{reduction}\right)$ in volt
$Li^+ + e \rightarrow Li(s)$	–3.05
$K^+ + e \rightarrow k(s)$	–2.93
$Na^+ + e \rightarrow Na(s)$	–2.71
$Mg^2 + 2e \rightarrow Mg(s)$	–2.36
$Al^3 + 3e \rightarrow Al(s)$	–1.66
$Zn^{2+} + 2e \rightarrow Zn(s)$	–0.76
$Fe^{2+} + 2e \rightarrow Fe(s)$	–0.44
$2H^+ + 2e \rightarrow H_2(s)$	0.00
$Cu^{2+} + 2e \rightarrow Cu(s)$	+0.34
$Ag^+ + e \rightarrow Ag(s)$	0.80
$Cl_2(g) + 2e \rightarrow 2Cl^-$	1.36
$F_2(g) + 2e \rightarrow 2F^-$	2.87

Application of Electrochemical Series

1. To claculate the emf of the cell

$E^0_{cell} =$ Standard reduction potential of cathode (RHE)- Standard reduction potential of anode(LHE).

In a cell, the electrode whose reduction potential is higher is made cathode & the other one the anode. If in a cell where is Zn and Cu electrodes, then copper electrode is made cathode $\left(E^0_{Cu^{2+}} = 0.31V\right)$ and zinc electrode is made anode $\left(E^0_{Zn^{2+}} = -0.76V\right)$.

Hence $E^0_{cell} = E^0_{cathode} - E^0_{anode} = 0.34\,V - (0.76)\,v = 1.10V$ (E^0 of Daniell cell)

Questions - Calculate the emf of the cell $Zn\,|\,Zn^{2+}\,||\,Ag^{+}\,|\,Ag$

Given $E_{Zn^{2+}}\,|\,Zn = -0.76\,v$

$E^0_{Ag^{+}|Ag} = +0.80v$

Here as reduction potential of silver electrode is more that of the electrode potential of Zn-electrode, the former is the cathode and the later is the anode.

$E^0_{cell} = E^0_{cathode} - E^0_{anode} = \left[0.80 - (-0.76)\right]V = 1.56V$.

2. To predict whether a particular redux reaction can occur or not

By calculating the EMF of the cell, of the emf value becomes positive, then the redox reaction will occur in the cell, but if the value comes to be negative, then no redox reaction will take place as

$\Delta G^0 = -nFE^0$, E^0 is positive, $\Delta G^0 = -\text{negative}$ i.e. the reaction spontaneous. Flow of e^- becomes also spontaneous.

$Zn(s) + Cu^{2+} \rightarrow Zn^{2+}(aq) + Cu$

$E^0_{cell} = E^0_{Cu^{2+}|Cu} - E^0_{Zn^{2+}|Zn} = 0.34 - (-0.76) = 1.10v$

Here zinc displaces copper from copper sulphate sollution.

But the reaction $Cu + Zn^{2+} \rightarrow Zn + Cu^{2+}$ will not occur

Because here $E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$= E^0_{Zn^{2+}|Zn} - E^0_{Cu^{2+}}\,|\,Cu$

$= -0.76v - (-0.34v) = -1.10v$. $\left(+\Delta G^0 = -nFE^0\right)$

Since here the emf of the cell comes to be negative no reaction takes place i.e. copper can not displace zinc from its salt solution.

3. To predict relative reactivity of elements :- Higher is the oxidation potential (lower the reduction potential) of a metal more easily it can lose electrons and hence greater is its reactivity. A metal with lower reduction potential can displace metals with higher reduction potential from their salt solution. So Mg and Zn displaces H_2 from dil H_2SO_4 but Cu cant displace H_2. Simulaly Zn having reduction potential (–0.76v) can displace copper from $CuSO_4$ solution. $CuSO_4$ solution. can't be preserved in a zinc vessel but $ZnSO_4$ in copper vessel.

NERNST EQUATION

1. For electrode potential :- The electrode potential of an electrode is called standard electrode potential of the concentration of the electolyte is 1(M) and temperature is 298K. But when the concentration of the electrolyte is different from 1M and the temperature is not 298K, then the electrode potential will be different from standard value. Acording to Nernst for an electrode reaction $M^{n+} + ne \rightarrow M$, the electrode potential

$$(E) = E^0 - \frac{RT}{nF}\ln\frac{[M]}{\left[M^{n+}\right]} \qquad \text{..... (1)}$$

where

E^0 = Standard electrode potential (From electro-chemical series)

R = Gas constant = 8.31 $Jk^{-1}mol^{-1}$

T = Temperature in Kelvin

F = One Faraday (96500 coulombs)

n = number of electrons involved in the electrode reaction.

Equation (1) can be written as $E = E^0 + \frac{RT}{nF}\ln\left[M^{n+}\right]$ or $E = E^0 + \frac{2.303RT}{nF}\log\left[M^{n+}\right]$

$$\boxed{E = E^0 + \frac{0.0591}{n}\log\left[M^{2+}\right]}$$

2. Nernst Equation for EMF of a Cell

Let us consider the example of the Daniel cell $Zn\left|ZnSO_4(aq)\right|CuSO_4(aq)\left|Cu\right.$

The electrode reaction for anode is $Zn(s) \rightarrow Zn^{2+}(aq) + 2e$ .... (1)

The electrode reaction for cathodes $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$ .... (2)

The cell reaction is $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

According Nernst equation the electrode potential of Zn | Zn^{2+} electrode is given by

$$E_{Zn^{2+}|Zn} = E^0_{Zn^{2+}|Zn} + \frac{RT}{2F}\ln\left[Zn^{2+}(aq)\right] \qquad \text{.... (3)}$$

Electrode potential for Cu^{2+} | Cu electrodes given by

$$E_{Cu^{2+}|Cu} = E^0_{Cu^{2+}|Cu} + \frac{RT}{2F}\ln\left[Cu^{2+}(aq)\right] \qquad \text{.... (4)}$$

$$\therefore \quad E_{cell} = E^0_{cathode} - E^0_{anode} = E^0{}_{Cu^{2+}|Cu} - E^0{}_{Zn^{2+}|Zn}$$

$$= \left\{E^0_{Cu^{2+}|Cu} + \frac{RT}{2F}\ln\left[Cu^{2+}(aq)\right]\right\} - \left\{E^0_{Zn^{2+}|Zn} + \frac{RT}{2F}\ln\left[Zn^{2+}(aq)\right]\right\}$$

$$= \left(E^0_{Cu^{2+}|Cu} - E^0_{Zn^{2+}|Zn}\right) + \frac{RT}{2F}\ln\frac{\left[Cu^{2+}(aq)\right]}{\left[Zn^{2+}(aq)\right]}$$

$$= E^0_{cell} - \frac{RT}{2F}\ln\left[\frac{Zn^{2+}(aq)}{Cu^{2+}(aq)}\right]$$

$$\boxed{E_{cell} = E^0_{cell} - \frac{0.0591}{2}\log\frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}}$$

For a general cell reaction $aA + bB \xrightarrow{ne} xX + yY$

Applying Nernst equation, we have $E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln \frac{[X]^x [Y]^y}{[A]^a [B]^b}$

At 298k, $E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[X]^x [Y]^y}{[A]^a [B]^b}$

Problem :-

1. Represent the cell in which the following reaction takes place and calculate the emf of the cedll if $E^0_{cell} = 3.17 \text{volt}$

$$Mg(s) + 2Ag^+(0.0001M) \to Mg^{2+}(0.130M) + +2Ag(s)$$

Ans. The cell is represented as $Mg(s) | Mg^{2+}(0.130) || Ag^+(0.0001M) | Ag$

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{\left[Mg^{2+}\right]}{\left[Ag^+\right]^2}$$

$$= 3.17v - \frac{0.0591}{2} \log \frac{(0.130)}{(0.0001)^2} = 3.17 - 0.21$$

or E_{cell} = 2.96v.

Q.2. Calculate the electrode potential of a copper wire dipped in 0.4m $CuSO_4$ solution at 25^0C. The standard electrode potential of copper is 0.34 volt.

Ans. The electrode reaction is $Cu^{2+} + 2e \to Cu$

Applying Nernst equation, $E = E^0 - \frac{0.0591}{2} \log \frac{\left[Cu\ \right]}{\left[Cu^{2+}\right]} \left(\because [Cu] = 1\right)$

or $E = 0.34 - \frac{0.0591}{2} \log \frac{1}{(0.1)}$

= 0.34 – 0.02955 = 0.31045v

Q.3. The emf of the following cell is found to be 0.20v at 298k.

$Cd | Cd^{2+}(?) || N_i^{2+}(2.0M) | Ni$

What is the molar concentration of Cd^{2+} ions to the solution

$\left(\text{Given } E^0_{Cd^{2+}|Cd} = -0.40v \text{ and } E^0_{Ni^{2+}|Ni} = -0.25v\right)$

Hence $E^0_{cell} = E^0_{cathode} - E^0_{anode} = -0.25 - (-0.40) = 0.15v$

Applying Nernst equation, $E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{\left[Cd^{2+}\right]}{\left[Ni^{2+}\right]}$

or $0.20 = 0.15 - \frac{0.0591}{2} \log \frac{\left[Cd^{2+}\right]}{2}$

or $\log\left[Cd^{2+}\right]-\log 2=-1.690$

or $\left[\log Cd^{2+}\right]=-1.690+0.3021=-1.3879$

or $\left[Cd^{2+}\right]=\text{anti}\log\bar{2}.6121=0.0409M.$

LECTURE - 22

Relation between Gibbs Free energy and cell potential

The electrical work done by a galvanic cell is equal to decrease in its Gibbs free energy. Hence if the emf of the cell is E and nF is the amount of charge passed and $\Delta_f G$ is the Gibbs energy of the reaction.

So $\Delta_f G=-nFE_{cell}$

For the reaction $Zn(s)+Cu^{2+}(log)\rightarrow Zn^{2+}(aq)+Cu$.

For the cell reaction $\Delta_f G=-2F\ E_{cell}\ (\because \text{Here } n=2)$

If the concentration of all the reacting species is unity, then we can write

$\boxed{\Delta G^0=-nFE^0}$

Here ΔG^0 is called standard free energy charge of the reaction.

Problem :

1. The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs free energy for the reaction $Zn(s)+Cu^{2+}(aq)\rightarrow Cu(s)+Zn^{2+}(aq)$

$\Delta G^0=-nFE^0=-2\times 96500\times 1.1$
$= -212,300\ kJ\ mol^{-1}$.

Relation between Equilibrium constant and free energy change

$$\Delta G^0=-RT\ln K_c=-2.303RT\log K_c$$

CORROSION :- The process of slowly eating away of the metal due to attack of atmospheric gases on the surface of the metal resulting into formation of compounds such as oxides, sulphides, carbonates, sulphates etc. is called corrosion. The examples of corrosion are rusting of iron, tarnishing of silver, development of green coating on copper and bronze.

Corrosion of iron, commonly known as rusting of iron occurs in presence of water and air. The electrochemical phenomenon behind the corrosion is as follows.

At a particular spot of an object made of iron oxidation takes place and that spot behaves as anode and we can write the reation.

Anode :- $2Fe(s)\rightarrow 2Fe^{2+}+4e^0, E^0_{Fe^{2+}|Fe}=-0.44v$

The electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H^+ (which is believed to be made available from H_2CO_3 formed due to dissolution of CO_2 from air into water

$$\text{i.e.}\ .\left.\begin{array}{l}H_2+CO_2\rightarrow H_2CO_3\\ H_2CO_3\rightarrow 2H^++CO_3^{2-}\end{array}\right)$$

This spot behaves as cathode with the reaction.

Cathode : $O_2(g) + 4H^+(aq) + 4e \rightarrow 2H_2O(l), E^0_{H^+|O_2|H_2O} = 1.23v$

The overall cell reaction is

$$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

$$E^0_{cell} = 1.67v.$$

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide (Fe_2O_3, xH_2O).

Corrosion causes damage to buildings bridges, ships and all objects made of iron and due to corrosion we lose crores of rupees every year.

The prevention corrosion is made by covering the surface of objects by paint or by some chemicals (i.e. bisphenol) and by covering the surface by electroplating with other metals which are not corroded in the atmosphere like Zn, Sn etc.

HYDROGEN - OXYGEN FULL CELL and its advantage

Fuel Cells :- The galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol etc. directly into electrical energy are called fuel cells. One of the most successful fuel cell that was used for providing electrical power in Apollo space programme is hydrogen oxygen fuel cell. This type of fuel cell consists of a porous carbon electrode in which suitable catalysts like finely divided pt or Pd are incorporated in them. Concentrated KOH or NaOH solution is placed between the electrodes to act as electrolyte. H_2 and O_2 gases are bubbled through the porous electrodes into NaOH or KOH solution.

The electrode reactions are as follows :-

Anode : $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e$

Cathode : $O_2(g) + 2H_2O(l) + 4e \rightarrow 4OH^-(aq)$

Overall reaction : $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

In this cells the reactants are fed continuously to the electrodes and the products are removed continuously from the electrolyte compartment.+

LECTURE - 23

UNIT- IV

CHEMICAL KINETIC

Rate of reaction :- It is the decrease of concentration of any one of reactants per unit time or increase in the concentation of any one of the products per unit time.

For the reaction $A \rightarrow B$

Rate of reaction = $-\frac{dA}{dt} = +\frac{dB}{dt}$

Unit of rate of reaction - moles / litre s^{-1} or moles / litre min^{-1}.

Average Rate of Reaction :- We know that the rate of a reaction is defined as the change in concentration of a reactant or product per unit time.

Consider a hypothetical reaction $A \rightarrow B$.

Let us suppose that $[A_1]$ and $[B_1]$ be the concentration of A and B respectively at time t_1 and $[A_2]$ and $[B_2]$ be the concentration of A & B respectively at time t_2.

So time interval $(\Delta t) = t_2 - t_1$

$\Delta[A] = [A_2] - [A_1]$ (Here Δt corresponds to large time interval)

$\Delta[B] = [B_2] - [B_1]$

$$\text{Rate of reaction} = \frac{\text{Rate of decrease in concentration of A}}{\text{time taken}} = \frac{-\Delta[A]}{\Delta t} \quad .... (1)$$

$$\text{and also rate of reaction} = \frac{\text{Rate of increase in concentration of B}}{\text{time taken}} = +\frac{\Delta[B]}{\Delta t} \quad .... (2)$$

Eq. (1) & (2) represent the average rate of reaction.

So $r_{(av)} = -\frac{\Delta[A]}{\Delta t} = +\frac{\Delta[B]}{\Delta t}$

Instantaneous rate of reaction

The instantaneous rate of reaction or rate of reaction at any instant of time is the rate of change of concentration of any one of the reactants or products at that particular instant of time.

The express the instantaneous rate of reaction a small interval of time (dt) is chosen at that particular instant of time during which the rate of reaction is supposed to be almost constant.

Hence instantaneous rate of reaction = $\frac{dx}{dt}$

For a raction $A \rightarrow B$.

$r_{instantaneous} = -\frac{d[A]}{dt} = +\frac{d[B]}{dt}$. (explain through graph)

Factors affecting the rate of reation :- The factors affecting rate of reaction are as follows :

(a) Nature of reactant
(b) Effect of concentration
(c) Presence of catalyst
(d) Temperature
(e) Surface area of reactant
(f) radiation

Rate law and specific reaction rate

Consider the general reaction $aA + bB \rightarrow Product$

According to law of mass action

rate of reaction $\alpha [A]^a [B]^b$

or Rate = $k[A]^a [B]^b$

However, experimentally, it is observed that the rate of this reaction may not depend upon 'a' moles of A & 'b' moles of B, but depends upon 'α' moles of A and β moles of B.

Hence rate $\alpha [A]^\alpha [B]^\beta$

or Rate = $k[A]^\alpha [B]^\beta$ .... (1)

The constant 'k' is called velocity constant or rate constant. The above expression is called *Rate law.*

Hence rate law is the expression which expresses the rate of reaction interms of molar concentration of the reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of that reactant on the balanced chemical equation.

If all the concentrations are taken as unity i.e., [A] = [B] = 1mole / litre, then

$\boxed{Rate = k,}$

Hence rate constant may be defined as the rate of the reaction when molar concentration of each reactant is taken as unity. For this reason the rate constant is called specific reaction rate.

Problem :-

1. The decomposition of N_2O_5 in CCl_4 at 318 k has been studied by monitoring the concentration of N_2O_5 in the solution. Initially the concentration of N_2O_5 is 2.33 mol / litre and after 184 minutes, it is reduced to 2.08 mole / litre. The reaction takes place according to the equation.

   $$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

   Calculate the average rate of reaction interms, of hours, minutes and seconds. What is the rate of production of NO_2 during this period.

Ans. Average rate = $\frac{1}{2}\left\{-\frac{\Delta[N_2O_5]}{\Delta t}\right\} = -\frac{1}{2}\left[\frac{(2.05-2.33)\text{mole / litre}}{184\,\text{min}}\right]$

$$= 6.79\times10^{-4}\,\text{mol / litre min}^{-1}$$

$$= \left(6.79\times10^{-4}\,\text{mol / litre mol}^{-1}\right)\times 60\,\text{min/ 1h}$$

$$= 4.07\times10^{-2}\,\text{mol L}^{-1}\text{ / h}$$

$$= 6.79\times10^{-4}\,\text{mol / litre min}^{-1}\text{ / 60s}$$

$$= 1.13\times10^{-5}\,\text{mol }\ell^{-1}\text{s}^{-1}$$

It may be written that

$$\text{Rate} = \frac{1}{4}\frac{\Delta[\text{NO}_2]}{\Delta t}$$

or $$\frac{\Delta[\text{NO}_2]}{\Delta t} = 6.79\times10^{-4}\text{mol L}^{-1}\text{ min}^{-1}\times 4 = 2.72\times10^{-3}\text{mol L}^{-1}\text{ min}^{-1}$$

2. Write the expression for the rate of reaction for the reaction

$$5\text{Br}^-(\text{aq}) + \text{BrO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$$

$$\text{Rate} = -\frac{1}{5}\frac{\Delta[\text{Br}]}{\Delta t} = -\frac{\Delta\left[\text{BrO}_3^-\right]}{\Delta t} = -\frac{1}{6}\frac{\Delta\left[\text{H}^+\right]}{\Delta t}$$

$$= \frac{1}{3}\frac{\Delta[\text{Br}_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

3. In a reaction $2\text{A} \rightarrow$ product, the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval.

Ans. Rate of reaction = $\frac{1}{2}\frac{\Delta[\text{A}]}{\Delta t} = \frac{1}{2}\frac{(0.5-0.4)}{10} = \frac{1}{2}\times\frac{0.1}{10} = \frac{0.01}{2} = 0.005\text{mol / litre min}^{-1}$

LECTURE - 24

Order of reaction

Consider the general reaction $\text{aA} + \text{bB} \rightarrow \text{Product}$.

Here 'a' and 'b' are the initial concentration of A & B respectively. If 'α' moles of A and 'β' moles of B react to form products then the rate law is $\text{rate} = \text{K}[\text{A}]^{\alpha}[\text{B}]^{\beta}$

The order of reaction = $\alpha + \beta$

Hence the order of reation may be defined as the sum of the exponents to which the molar concentrations in the rate law equation are raised to express the observed rate of reaction. or it may be defined as the number of molecules of the reactants whose concentration changes during the course of reaction.

Types of order of reaction

1. **Zero order reaction -** Here rate of reaction does not depend upon the concentration of reactants

Example - Photolysis of HCl.

$$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \xrightarrow[\text{surface of water}]{h\nu} 2\text{HCl}$$

Here Rate = $\text{k}[\text{H}_2]^0[\text{Cl}_2]^0 = \text{k}$.

2. **First order reaction :-** Ex (1) Dissociation of N_2O_5

$$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$$

Rate of reaction $\alpha[N_2O_5]$ or $\text{rate} = k[N_2O_5]^1$

(2) Acid hydrolysis of ester $CH_2COOC_2H_5 + H_2O \xrightarrow{H_2SO_4}$ $CH_3COOH + C_2H_5OH$

$\boxed{\text{Rate of reaction} = k[CH_3COOC_2H_5]}$ It zero order with respect of H_2O

3. **2nd order reaction :-** Alkaline hydrolysis of saponification of ester

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

Rate of reaction = $k[CH_3COOC_2H_5]^1[NaOH]^1$.

order of reaction = 1 + 1 =2.

4. **Fractional Order reaction :-** For Decomposition of Acetaldehyde the order of reaction is 1.5.

$$CH_3CHO \xrightarrow{723k} CH_4 + CO$$

Rate of reaction = $k[CH_3CHO]^{1.5}$

Molecularity :- The number of molecules which take part in the rate determining step of the reaction is called the molecularity of reaction.

(i) Unimolecular reaction - $N_2O_5 \xrightarrow{\Delta} N_2O_4 + \frac{1}{2}O_2$

$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

(ii) Bimolecular reaction -

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

(iii) Termolecular reaction - $2SO_2 + O_2 \rightarrow 2SO_3$

Difference between order of reaction and molecularity

Order of reaction	**Molecularity**
1. It is sum of the exponents of the molar concentration in the rate law equation or the sum of concentration terms on which the rate of reation actually depends	1. The number of molecules of the reactants which take part in the rate determining step of the reactaion.
2. It may be zero, whole number or fraction	2. It is always a whole number. It cannot be zero or a fraction.
3. It can be determined experimentally	3. It can be calculated by simply adding the molecules in the slowest step of reaction.
4. For simple reactions the order of reaction may not be equal to the number of molecules of the reactants as seen from balanced equation.	4. For simple reactions, the molecularity is obtained by adding the number of molecules in the balanced equation.

Ex. $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$ order of reaction = 1.	
5. Order of reaction pertains to whole of the reaction (reactant.product) irrespective of inter mediates.	5. Molecularity pertainst to each stp, not as a whole of the reaction.

Difference between rate of reaction and reaction rate constant or specific rate constant

Rate of reactions	**Reaction Rate Constant**
1. Rate of reaction is the change in concentration of a reactant or product per unit time.	1. It is a constant of proportionality in the rate law equation and is equal to the rate of reaction when the molar concentration of each of the reactants is unity.
2. The rate of reaction at any instant of time depends upon the molar concentration of reactants at that time.	2. The rate constant is a constant for a particular reaction and is independent of concentration of the reactants
3. Its unit is always mol litre^{-1} time^{-1}	3. Its unit depends upon the order of reaction.

LECTURE - 25

Integrated rate expression for zero order reaction

Consider the general reaction $A \rightarrow \text{Product}$

For a zero order reation, $\text{Rate} = \frac{d[A]}{dt} = k[A] = k.$

or, $dA = -kdt$

Integrated both sides, we get $[A] = -kt + I$ .... (1)

where I = constant of integration

At $t = 0, [A] = [A_0]$

So, $[A_0] = -k.0 + I$

or $I = [A_0]$

Putting the value of I in equation (1) we get

$[A] = -kt + [A_0]$

or $kt = [A_0] - [A]$

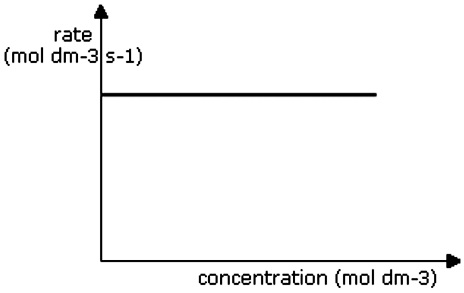
or $\boxed{k = \frac{1}{t}[A_0] - [A]}$

This is the expression for rate constant for zero order reaction.

Characteristics of zero-order reaction

(i) Unit of rate constant is mole litre^{-1} time^{-1}. (same as rate of equation)

(ii) As the rate of reaction is independent of concentration, so plot of rate versus concentration will be a straight line parallel to concentration axis.



(iii) **Half-life period :-** Half -life period is the time during which half of the reactants are converted to products.

We know $k = \frac{1}{t}[A_0] - [A]$ .... (2)

when $t = t_{\frac{1}{2}}, [A] = \frac{[A_0]}{2}$

So putting these values in equation (2) we get

$$t_{1/2} = \frac{[A_0] - [A_0]/2}{k} = \frac{[A_0]}{2k}$$

or $\boxed{t_{1/2} = \frac{[A_0]}{2k}}$

So half-life period of a zero order reaction is directly proportional to initial concentration.

Integrated Rate Equation for First Order Reaction

For a first order reaction the concentration of only one reactant changes during the course of reaction.

Let us consider a general first order reaction

$A \rightarrow \text{Pr oducts.}$

Let initial concentration of 'A' at the beginning i.e. at 't' = 0 is 'a' mole / litre and 'x' mole/litre is converted to products in time 't'. Hence concentration of reactant (A) after time 't' = (a – x) mole / litre.

According to law of mass action, I

Rate of reaction $\alpha(a - x)$

or $-\frac{d(a-x)}{dt} \alpha (a - x)$

or $\frac{dx}{dt} = k(a - x)$

or $\frac{dx}{a-x} = k\,dt$ (on rearrangement) .... (1)

Integrating equation (1) both sides we get .... (2)

$-\ln(a-x) = kt + I$, where I = constant of integration

In the beginning when t = 0, x = 0 (as no reactant has reacted)
Putting this value in eq. (2), we get
$-\ln(a-0) = k.0 + I$

or $I = -\ln a$ .... (3)

Putting the value of I, in eq. (2), we get
$-\ln(a-x) = k.t - \ln a$

or $k.t = \ln a - \ln(a-x)$

or $\boxed{k = \frac{1}{t}\ln\frac{a}{a-x}} = \frac{1}{t} \times 2.303 \log\frac{a}{a-x}$ .... (4)

Equation (4) is the rate expression for 1st order reaction.

Characteristics of 1st order reaction

1. Unit of rate constant = time^{-1} i.e., sec^{-1}, min^{-1} or hr^{-1}.
2. Half-life period :-

we know $k = \frac{1}{t}\ln\frac{a}{a-x}$

when $t = t_{1/2}$, $x = a/2$

Hence, $k = \frac{1}{t_{1/2}}\ln\frac{a}{a-a/2}$

$$t_{1/2} = \frac{1}{k}\ln\frac{2a}{a}$$

or $t_{1/2} = \frac{1}{k}\ln 2 = \frac{1}{k} \times 2.303 \log 2$

$$\boxed{t_{1/2} = \frac{0.693}{k}}$$

From this expression it is obvious that the half life period of a first order reaction is independent of initial concentration.

Problem :

1. Show that the time required for the completion of 3/4th of a reaction of first order is twice the time required for completion of half-of the reaction.

Ans. $t = \frac{1}{k} \times 2.303 \log\frac{a}{a-x}$ or

when $t = t_{1/2}$, $x = a/2$ and when $t = t_{3/4}$, $x = 3a/4$

So $t_{1/2} = \frac{1}{k} \times 2.303 \log\frac{a}{a-a/2} = \frac{1}{k} \times 2.303 \log 2$ .... (1)

$$t_{3/4} = \frac{1}{k} \times 2.303 \log \frac{a}{a - 3a/4} = \frac{1}{k} \times 2.303 \log 4 = \frac{2 \times 2.303 \log 2}{k} \qquad .... (2)$$

Since are same.

$$\therefore \frac{t_{3/4}}{t_{1/2}} = \frac{\left(2 \times 2.303 \log^{2}\right)}{\left(2.303 \log^{2}\right)k} = 2$$

or $\boxed{t_{3/4} = 2 \times t_{1/2}}$

2. A first order reaction takes 69.3 minutes for 50% completion. How much time will be needed for 80% completion.

For a first order reaction, $t = \frac{2.303}{k} \log \frac{a}{a - x}$

For 50% completion, $t_{50\%} = \frac{2.303}{k} \log \frac{100}{100 - 50}$

$$= \frac{2.303}{k} \log 2 \qquad .... (1)$$

For 80% completion $t_{80\%} = \frac{2.303}{k} \log \frac{100}{100 - 80} = \frac{2.303}{k} \log 5 \qquad .... (2)$

Dividing eq. (2) by (1), we get

$$\frac{t_{80\%}}{t_{50\%}} = \frac{2.303}{k} \log 5 / \frac{2.303 \log 2}{k}$$

or $\frac{t_{80\%}}{t_{50\%}} = \frac{\log 5}{\log 2}$

For 50% change, the time is 69.3 minutes.

Hence $t_{80\%} = 69.3 \times \frac{\log 5}{\log 2} = \frac{69.3 \times 0.669}{0.301} = 160.9 \, \text{min}$

LECUTRE - 26

Concept of Collision Theory - According to this theory the reactant molecules are assumed to be hard spheres and reaction is assumed to occur when molecules collide with each other. The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (z). Another factor that affects the rate of chemical reactionis activation energy.

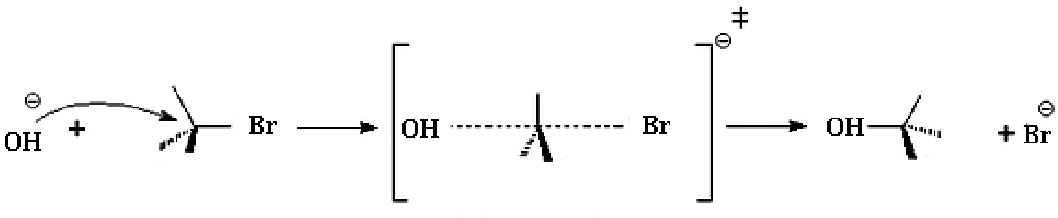
For a bimolecular reaction $A + B \rightarrow \text{Product}$,

the rate of reaction = $ZS_{AB}\ e^{-Ea/RT}$ .... (1)

where Z_{AB} represents the collision frequency of reactants A and B and $e^{-Ea/RT}$ represents the fraction of molecules with energies equal to or greater than Ea. Comparing with Arrhenius equation $k = Ae^{-Ea/RT}$ we say that A is related to collision frequency. Equation (1) is satisfactory for atomic species or simple molecules but fails for complex molecules deviations are observed.

The reason is that all collision donot lead to the formation of products. The collisions in which molecules collide with sufficient kinetic energy called thresh hold energy and proper orientation so as to facilitate breaking of bonds between reacting species and formation new bonds to form products are called as effective collisions.

For example, formation of methanol from bromomethane depend upon the orientation of reactant molecules as shown in the figure.



S_N2 mechanism

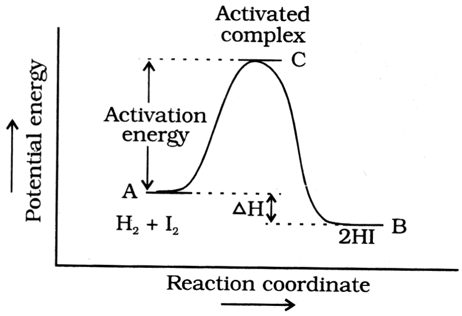
To account for effective collisions anther factor P, called the steric factor in introduced. It takes into account the fact that in a collision molecules must be properly oriented.

i.e. Rate = $PZ_{AB}e^{-E/RT}$

Activation Energy :- According to collision theory a reaction takes place due to collision of reacting molecules with each other. All the collisions do not lead to chemical reaction, but only those collisions in which the colliding molecules have more than a particular value are effective in bringing about reaction.

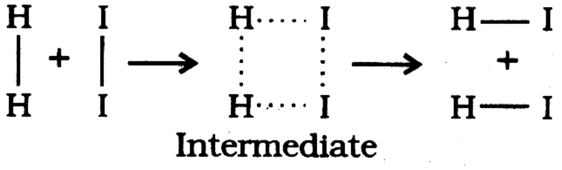
The minimum energy which the colliding molecules must have inorder that the collision between them may be effective is called Threshold energy. At room temperature most of the reactant molecules have energy less than the threshold value. By supplying energy in the form of heat and light the reactant molecles absorb the energy and their energy becomes equal to or greater than the threshhold value is called activation energy.

Activation Energy = Threshhold Energy – Average kinetic energy of the reactants



Let us consider the simple reaction $H_2(s)+I_2(s) \rightarrow 2HI(s)$

By absorbing energy H_2 and I_2 molecules collide and form an intermediate called activated complex which exists for a short time and then breaks up to form two molecules of HI.



In the diagram energy E_1 is the activation energy for the forward reaction and energy E_2 is the activation energy for the backward reaction.

When $E_2 > E_1$, the reaction is exothermic and when $E_1 < E_2$, the reaction is endothermic.

Problem

1. For the reaction $X \rightarrow Y, \Delta H = -80\text{kcal}$ and Ea = 27.0 kcal. Find E_a for reverse reaction.

Ans. For the reaction = –80 kcal i.e. $E_p - E_r = -80$ kcal

Activation energy for backward reaction = (80 + 27) kcal = 107 kcal

2. For a reaction $A \rightarrow B$, the average energies of A and B are 30 and 60 kcal respectively. Energy of activation for backward reaction is 93 kcal. Findout energy of activation for the forward reaction and ΔH for the reaction.

Ans. $E_r = 30$ kcal & $E_p = 60$ kcal

$E_2 = 93$ kcal

ΔH for the reaction = $E_p - E_r$ = (60 – 30) kcal = 30 kcal.

Energy of activation for forward reaction = (93 + 30) kcal = 153 kcal

LECTURE - 27

Arrhenius Equation :- The effect of temperature on the rate of a reaction and hence the rate constnat ‘k’ was proposed by Arrhenius. Arrhenius equation is written as $k = Ae^{-Ea/RT}$.

where A is constant called frequency factor (because it gives the frequency of binary collisions of the reacting molecules per second per litre), E_a is the energy of activation, ‘R’ is the gas constant and T is the absolute temperature.

Derivation

According to van’t Hoff’s equation

$$\frac{d\ln K_e}{dt} = \frac{\Delta E}{RT^2} \quad \text{.... (1)}$$

where K_e is the equilibrium constant = $\frac{k_1}{k_2}$, where k_1 and k_2 are the rate constant for forward and backward reactions.

$$\frac{d\ln \frac{k_1}{k_2}}{dt} = \frac{\Delta E}{RT^2}$$

or $$\frac{d\ln k_1}{dt} - \frac{d\ln k_2}{dt} = \frac{E_1}{RT^2} - \frac{E_2}{RT^2} \left(\because \Delta E = E_1 - E_2\right) \quad \text{.... (2)}$$

splitting eq. (2) we get,

Hence. $\frac{d\ln k_1}{dt} = \frac{E_1}{RT^2}$ and $\frac{d\ln k_2}{dt} = \frac{E_2}{RT^2}$

In general $$\boxed{\frac{d\ln k}{dt} = \frac{E}{RT^2}} \quad \text{.... (3)}$$

On integrating eq. (1), we get

$$\int \frac{d\ln k}{dt} = \int \frac{E}{RT^2}$$

or $$\int d\ln k = \int \frac{E}{RT^2}.dt$$

or $$\ln k = -\frac{E}{RT} + \text{constant} \qquad .... (4)$$

or $$\log k = -\frac{E}{2.303RT} + \text{constant} \qquad .... (5)$$

So plot of log k vs $\frac{1}{T}$ gives a straight line with slope -E/2.303R, where E is the activation energy from eq. (4), we have $\boxed{k = Ae^{-E/RT}}$

This equation is known as Arrhenius equation.

Calculation of activation Energy from Arrhenius Equation

Arrhenius equation is $k = Ae^{-Ea/RT}$ .... (1)

Taking logarithm of both sides of equation (1), we get

$$\ln k = \ln A - \frac{Ea}{RT} \qquad .... (2)$$

If the values rate constants at temperature T_1 and T_2 are k_1 and k_2 respectively, then we have

$$\ln k_1 = \ln A - \frac{Ea}{RT_1} \qquad .... (3)$$

$$\ln k_2 = \ln A - \frac{Ea}{RT_2} \qquad .... (4)$$

Substrating equation (4) from (3), we get

$$\ln k_2 - \ln k_1 = \frac{-Ea}{RT_2} - \left(-\frac{Ea}{RT_{11}} \right)$$

or $$\ln \frac{k_2}{k} = \frac{Ea}{RT_1} - \frac{Ea}{RT_2} = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

or $$\log \frac{k_2}{k_1} = \frac{Ea}{2.303R}\left(\frac{T_2 - T_1}{T_1 \ T_2} \right) \qquad .... (5)$$

Knowing the values rate constant k_1 and k_2 at two different temperatures T_1 and T_2, the activation energy > (E_a) can be calculated.

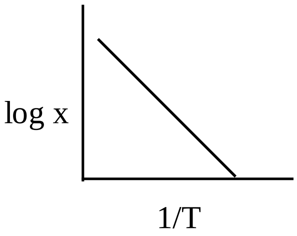
Validity Arrhenius Equation

Arrhenius equation is $k = Ae^{-Ea/RT}$

Taking logarithm $\ln k = -\frac{Ea}{RT} + \ln A$

or $\quad \log k = \frac{-Ea}{2.303RT} + \log A$

This equation is in the form, y = mx + c, i.e. the equation of a straight line. This is the plot of log x ~ 1/T is C straight line, the validity of equation is confirmed.



From the above equation we have slope of line $= -\frac{Ea}{2.303R}$.

Thus, measuring the slope of the line, the value of Ea can be calculated.

Problem

1. The rate of a particular reaction doubles when temperature changes from 27^0C to 37^{0C} calculate the energy of activation of such a reaction.

Ans. $\log \frac{k_2}{k_1} = \frac{Ea}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$

$$\log \frac{2k}{k} = \frac{E_0}{2.303 \times 8.314 jK^{-1} mol^{-1}} \times \frac{(310 - 300)k}{300k \times 310k}$$

or $\quad \log 2 = \frac{Ea}{2.303 \times 8.314} \times \frac{10}{300 \times 310 (Jmol^{-1})}$

$\therefore$ On solving E_a = 44.13 kJ mol^{-1}

2. The rate constant of a reaction is $1.2 \times 10^{-3} sec^{-1}$ at 30^0 and $2.1 \times 10^{-3} sec^{-1}$ at 40^0C. Calculate the energy of activation of the reaction.

Ans. $\log \frac{k_2}{k_1} = \frac{Ea}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$

or $\quad \log \frac{2.1 \times 10^{-3} sec^{-1}}{1.2 \times 10^{-3} sec^{-1}} = \frac{Ea}{2.303 \times 8.314 Jk^{-1} mol^{-1}} \times \frac{(313 - 303)r}{313K \times 303K}$

$$\log \frac{2.1 \times 10^{-3} s^{-1}}{1.2 \times 10^{-3} s^{-1}} = \frac{10}{3.3 \times 310 J\ mol^{-1}}$$

On solving we get Ea = 44.13 kJ mol^{-1}

LECTURE - 28

UNIT- V

SURFACE CHEMISTRY

Adsorpation :- The phenomenon of attracting and retaining the molecules of a substance on the surface of liquid or solid resulting into higher concentration of the molecules on the surface is called adsorption.

Adosorbent and adsorbate :- The substance which is adsorbed on the surface is called adsorbate and the substance on which it is adsorbed is caleld adsorbent.

Desorption :- Removal of adsorbed substance from the surface is called desorption, which can be brought about by heating or reducing the pressure.

Occlusion :- The adsorption of gases on the surface of the metal is called occlusion.

Types of Adsorption :-

(i) Physical adsorption or physisorption

(ii) Chemical adsorption or chemisorption

1. Physical adsorption :- When a gas is adsorbed on the surface of a solid by vander Waal forces without resulting into the formation of any chemical bond between the adsorbate and adsorbent, it is called physical adsorption.

Characteristics of Physical adsorption

(i) Lack of specificity - A given surface an adsorbent does not show any preference for a particular gas is the type of adsorption.

(ii) Nature of adsorbate - Easily liquifiable gases with high critical temperature are adsorbed more strongly because they have stronger vander Waals forces of attraction, near the critical temperature. Thus 1g of activatived charcoal adsorbs more sulphur dioxide than methane.

(iii) Reversible nature :- Physical adsorption of a gas by a solid is generally reversible. Thus

$$\underset{(\text{Adsorbent})}{\text{Solid}} + \underset{(\text{Adsorbate})}{\text{Gas}} \rightleftharpoons \text{Gas} - \text{solid} + \text{heat}$$

(iv) Surface area of adsorbent - The extent of adsorption increases with the increase in surface area of absorbent. So finely divided metal and charcoal powder are good adsorbents.

(v) Enthalpy of Adsorption :- Physical adsorption is an exothermic process but enthalpy of adsorption is quite low (20 – 40 kJ mol^{-1}). This is because of weak Vander Waal's force of attraction between gas molecules and solid surface.

(2) Chemical Adsorption :- When the gas molecules or atoms are held to the solid surface by chemical bonds, the adsorption is termed as chemical adsorption or chemisorption. Chemical bond may be covalent or ionic in nature.

Characteristics of Chemisorption

(i) High specificity - Chemisorption is highly specific in nature because it occurs only if there is a chance of chemical bond formation between the adsorbate and adsorbent. For example - Oxygen will be chemisorbed only on those solid adsorbent (i.e. carbon or metal) with which it can form oxides.

(ii) Nature of adsorbate :- The adsorbate should form chemical bond with the adsorbent.

(iii) Irreversible nature - Chemisorption involves compound formation and is usually irreversible.

(iv) **Surface area of adsorbent -** Like physical adsorption, chemisorption also increases with increase in surface area of adsorbent.

(v) **Enthalpy of adsorption -** Enthalpy of chemisorption is high (80 – 240 kJ mol^{-1}) as it involves chemical bond formation.

Factors affecting adsorption of Gases on solids

The factor affecting adsorption of gases on solids are as follows

1. Nature and surface area of adsorbent
2. Nature of the gas adsorbed
3. Temperature
4. Pressure
5. Activation of solid adsorbent

Applications of Adsorption

- (i) Removal of poisonous gases by using gas mask.
- (ii) Removal of colouring matter
- (iii) Creation of high vacuum
- (iv) Chromatic purification of compounds
- (v) Removal of hardness of water
- (vi) In heterogeneous catalysis
- (vii) In Analytical chemistry
- (viii) In Medicines

LECTURE - 29

Catalyst :- Catalyst is a substance which can change the speed fo a chemical reaction without itself undergoing any change in mass and chemical composition at the end of the reaction and the phenomenon is known as catalysis. The catalyst for decomposition of $KClO_3$ to O_2 is manganese dioxide.

Positive and Negative Catalysis :- If a catalyst increases the speed of a chemical reation it is called a positive catalyst and the phenomenon is called positive catalysis. On the other hand if a catalyst retards the speed of a chemical reaction, it is called a negative catalyst and the phenomenon is called negattive catalysis.

Types of Catalysis :- These are of two types (i) Homogenous catalysis and (ii) Heterogenous catalysis.

1. **Homogenous Catalysis :-** When the reactant and catalyst are in the same phase (i.e. both liquid or gas), the process is said to be homogenous catalysis.

Example - (i) Oxidation of SO_2 to SO_3 with oxygen in presence of Nitric oxide catalyst

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

(ii) Hydrolysis of ethyl acetate by dil. H_2SO_4 or dil. HCl

$$CH_3COOC_2H_5(l) + H_2O(l) \xrightarrow{dil.H_2SO_4} CH_3COOH + C_2H_5OH$$

(iii) **Hydrolysis of sugar solution -** the presence dil H_2SO_4

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{dil\ H_2SO_4} \underset{Glucose}{C_6H_{12}O_6(aq)} + \underset{Fructose}{C_6H_{12}O_6(aq)}$$

2. Heterogenous Catalysis

When the reactants and catalyst are of different phases, the process is called heterogenous catalysis.

Example - (i) Oxidation SO_2 into SO_3 inpresence of platinum

$$2SO_2(g) + O_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$$

(ii) $N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$ (Haber's process of manufacture of NH_3)

(iii) Oxidation of NH_3 to Nitric Oxide in presence of platinum gauze in Ostwald's process

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt(s)} 4NO(g) + 6H_2O(g)$$

(iv) In stomach, the pepsin enzyme converts proteins into peptides while in intenstine pancreatic trypsin converts proteins into aminoacids by hydrolysis.

(v) Conversion of milk to curd by the enzyme lactobacilli.

Activity of a solid catalyst :- The activity of a catalyst depends upon the strength of chemisorption to a large extent. The reactants get adsorbed strongly on the catalyst to become active. By activity of the catalyst we mean its capacity to increase the speed of the chemical reaction. Combination of H_2 and O_2 in the presence of Pt - catalyst to form water with explain. In the absence of catalyst. They do not combine.

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O.$$

Selectivity of Solid Catalyst :- By selectivity of a catalyst we mean its ability to direct the reaction to form particular product. Example - starting with H_2 and CO, we get different products in presence of different catalysts.

(i) $CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$

(ii) $CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO-Cr_2O_3} CH_3OH(g)$

(iii) $CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$

From the above reactions it can be concluded that a catalyst is highly selective in nature i.e. a given substance can act as a catalyst only in a particular reaction and not for all the reactions.

LECTURE - 30

Crystalloids - The substances like common salt, sugar, urea etc. which are obtained in Orystalline form and in dissolved state diffuse readity - through the parchment membrane are called orystalloids.

Colloids - The substances like starch, gum, gelatine, albumin etc. which are non-Crystalline in nature and in dissolved state donot diffuse through the parchment membrane are called colloids.

The solutions formed by crystalloids are called True solution and the substances formed by colloids are called colloidal solutions.

Distinction between True solution, Collidal solutions and suspensions

True solution	Colloidal solution	Susspensions
(i) Homogenous	(i) Heterogenous	(i) Hetergenous
(ii) Particle size less than 1nm	(ii) Particle size lies between 1nm to 1000nm	(ii) Particle size is more than 1000 nm (i.e. > 10000 A^0).
(iii) Passes through ordinary filter paper and parchment membrane.	(iii) Passes through ordinary fitter paper but not throught	(iii) Donot pass either through ordinary fitter paper or parchment membrane
(iv) Particles are invisible	(iv) Particles are visible under ultramicroscope.	(iv) Particles are visible in naked eye and also under microscope.
(v) Donot settle	(v) Donot settle	(v) Settle on standing.

Tyndal Effect - If a strong converging beam of light is passed through a colloidal solution placed in a dark room, the path of the beam gets illuminated with a bluish light when viewed at right angles to the direction of the passage of light. The path of the light becomes visible due to scattering of light by the colloidal particles. This phenomenon was observed by Tyndal in 1869 and is called Tyndal effect.

Hence Tyndal effect may be defined as the scattering of light by the colloidal particles present in a colloidal solution.

The illuminated path of the beam is called Tyndal Cone - Tyndal effect is observed only when the following two conditions are satisfied.

(i) The diameter of the dispersed particles is not much smaller than the wavelength of the light used and

(ii) The refraction indices of the dispersed phase and the dispersion medium differ greatly in magnitude.

Brownioan movement - When colloidal solutions were viewed under a powerful ultramicroscope, the colloidal particles appear to be in a state of continuous Zig-zag motion. This motion was first observed by the British botanist Rober Brown and is known as Brownian movement. This motion is independent of the nature of the colloidal particles but depends on the size of the particles and viscosity of the solution. Small the size and lesser the viscosity faster is the motion. The Bromian movement is due to the bombardment of the particles by the molecules of the dispersion medium. Browmian movement does not permit the colloidal particles to settle and is responsible for the stability of colloidal solution.

LECTURE - 31

Electrophoresis - The positive or negative charge of the colloidal particles can be shown by the process of electrophoresis which involves the movement of colloidal particles towards one or the other electrode when placed under the influence of an electric field.

The movement of colloidal particles under the influence of an electric field is called electrophoresis or cataphoresis. As soon as the colloidal particles react the oppositely charged electrode, they get neutralised and hence are coagulated.

Coagulation or Flocculation :-

Coagulation is the process of aggregating together the colloidal particles so as to change them into large sized particles which ultimately settle as a precipitate.

Coagulation is generally brought about by the addition of electrolyte. When the electrolyte is added to a colloidal solution, the particles of sol take up the oppositely charged ions and gets neutralized. The neutral particles then start accumulating to for large size particles which settle down. The ion responsible for neutralizing the charge of colloidal particles is called coagulating ion or flocculating ion.

The minimum amuont of electrolyte (millimoles) that must be added to one litre of a colloidal solution so as to bring about complete coagulation is called coagulation or flocculation value of the electrolyte. The smaller is the coagulation value of an electrolyte, greater is its coagulating power.

EMULSION - An emulsion is a colloidal dispersion in which both the dispersed phase and the dispersion medium are imiscible liquid.

An emulsion is prepared by shaking strongly the mixture of two liquids in presence of an emulsifier, which stabilize the emulsion. The emulsifying agents or emulsifiers are usually soaps of various kinds, lyophilic colloids (protein, gum etc.)

Types of emulsions

(i) Emulsion of oil-in-water (o/w) - In it the dispersed phase is oil and water is the dispersion medium. Example - (i) Milk is an emulsion of liquid fat dispersed in water (ii) Vanishing cream

(ii) Emulsion of water-in-oil (w/o) - In it the dispersed phase is water and the dispersion medium is oil. Example - Cod liver oil, butter, cold cream.

Classification of Colloids

1. Based on interaction between dispersed phase and dispersion medium - On this basis colloidal solutions are of two types, namely lyophilic and lyphobic. If water is the dispersion medium, the terms are hydrophilic and hydrophobic.

(a) Lyophilic Colloids :- In lyophic colloids there exists strong attraction between dispersed phase and dispersion medium. Colloidal sols directly formed by mixing substances like gum, gelatine, starch, etc. with a suitable liquid are called lyophilic sols.

When the dispersed phase is separated from the dispersion medium (say by evaporation), the sol can be made again by simply remixing with the dispersion medium and shaking for this sols are called reversible sol.

(b) Lyophobic Colloids :- In these colloids there doesnot exist any interaction attraction between dispersed phase and dispersion medium. Substances like metals, their sulphides etc. when simply mixed with the dispersion medium donot from the coloidal solution. Their colloidal sols can be prepared only by special methods. Such sols are called lyophobic sols. These sols are readily precipitated (or coagulated on addition of a small amount of electrolyte, by heating or by shaking and so they are not stable. Once precipitated, they donot give back the colloidal sol by simple addition of dispersion medium. Hence these sols are also called irreversible sols.

2. Classification based on the type of particles of the dispersed phase :- These are multimolecular, macromolecular and associated colloids.

(a) **Multimolecular Colloids -** When on dispersion of a subsance in the dispersion medium, large number of atmos or smaller molecules of the substance (with diameter less than 1nm) aggregate together to form species having size in the colloidal range, the species thus formed are called multimolecular colloid. Example - Gold sol, sulphur sol.

(b) Macromolecular colloids :- When certain substances having big size molecules, called macromolecules, having larger molecular masses are dissolved in a suitable liquids, they form a solution in which the molecules of the substance i.e. the dispersed particles have size in the colloidal range, such substances are called macromolecular colloids.

Example - These macromolecular substances are usually polymers with high molecular masses. Naturally occuring macromolecules are starch, cellulose, proteins, enzymes and gelatine. Artificially synthesized macromolecules are polythene, nylon, polystyrene, synthetic rubber.

HOME ASSIGNMENT

(a) Collaidal solution is hetrogeneous. It consists of _______ and _______.

(b) A mixture of collaid and crystallid is separated by __________.

(c) The optical property of colloidal solution is called ________ effect.

(d) Gdd sol is ______ charged sol.

(e) The electrical property of colloidal solution is called __________.

(f) _____ provides stability to colloidal solution.

(g) Cold cream is –type of emulsion.

(h) 1f liquid dispersed in solid, the colloidal system is called ________.

Lecture - 32, 33, 34

UNIT - VI

GENERAL PRINCIPLE AND PROCESSES OF ISOLATION OF ELEMENTS

Metals available in the form of

(i) Free state Pt, Ag, Au, Cu

(ii) Mineral. compounds of metal with impurities
e.g. zincite (ZnO), Horn silver (AgCl), cuprite (Cu_2O) etc.

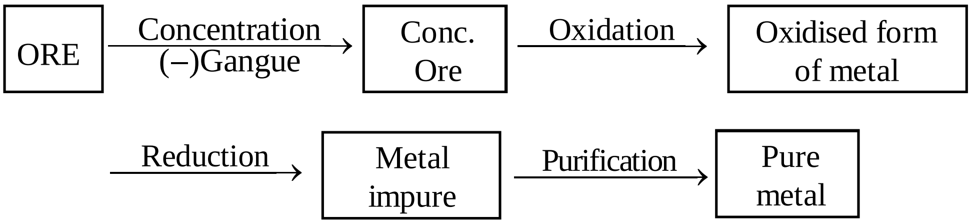
(iii) Ores - Naturally occuring substance from which metal may be extracted economically & profitably.

Galena (PbS, copper glance (C_2S), Zinc oxide (ZnO)

Calcium phosphate, $Ca_3(PO_4)_2$ etc.

Thus, all ores are minerals, but all minerals are not ores.

Metallurgy The process or processes by which metal is extracted from its suitable ore is called metallurgy.



(a) Concentration of the ore

The removal of wastearthy or srtony materials called gangue or matrix from the ore called concentration.

This can be affected by many processes like :

(i) Breaking and crushing : converted to small lumps by erusters etc.

(ii) Grinding and pulverised - converted to very fine state.

(iii) Washing: To remove lighter waste materials.
Iron ore, tin stone and native ores of Au, Ag etc. concentrated by this process.

(iv) **Froth floatation process**
Sulfide ore, eucalyptus oil or turpentine & water are agitated violently by air. Sulfide ore get preferentially welted compared to gangue materials. Sulfide ore sticks to the froth & floates on the surface leaving the gangue behind in the tank.

→ Pine oils, fatty acids, xanthates enhence non-wettability of the mineral particles.

→ Cresoles. aniline etc. stabilies the froth.

→ Depressants : To separate two sulfides. e.g. NaCN is used as depressant for ZnS, & PbS to come with froth.

$$4NaCN + ZnS \longrightarrow Na_2[Zn(CN)_4] + Na_2S$$

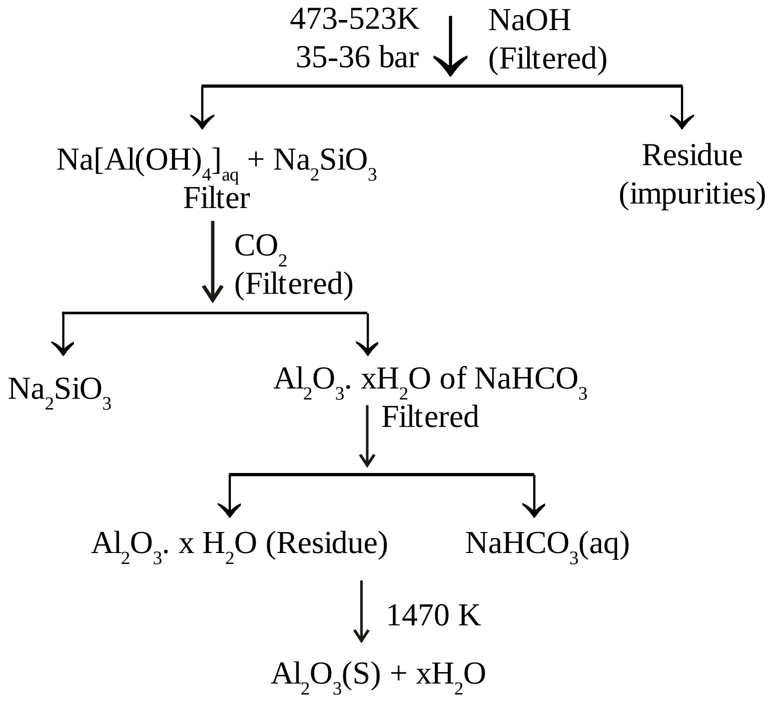
This complex is formed on the surface of ZnS preventing it to go with the froth.

(v) **Magnetic separator**
Non magnetic impurity (Tin stone-SnO_2) (gangue) can be separated from magnetic ore ($FeWO_4$ – wolfram) using magnetic pulley.

(vi) **Leaching :** The powdered ore is heated with suitable chemical to dissolve the ore but not the impurities.

e.g. (a) Leaching: (Alumina from bauxcite:

(ore containing $Al_2O_3 + SiO_2$) + Impurity



(b) Leaching of silver and gold :

Leaching reagent - NaCN

$$Ag_2S + 4\,NaCN \rightarrow 2Na\left[Ag\left(CN\right)_2\right] + Na_2S$$

$$\downarrow Zn$$

$$Na_2\left[Zn\left(CN\right)_4\right] + 2\,Ag\downarrow$$

Sodium tetracyanido zincate (II)

For native gold Leaching reagent KCN

$$4Au + KCN + O_2 + 2H_2O \rightarrow 4K\left[Au\left(CN\right)_2\right] + 4\,KOH$$

$$\downarrow Zn$$

$$K_2\left[Zn\left(CN\right)_4\right] + 2Au\downarrow$$

(b) Conversion of the concentrated ore into metallic oxide or de-electronation of ores.

The concentrated ore present as hydrated oxide (hydroxide) carbonates and sulfides. The following two methods are used for conversion of concentrated ore into their respective oxide.

1. **Calcination :** Process of conversion an ore to its oxide by heating strongly below its mp. either in absence or limited supply of air. During this process following changes occur ____

* Moisture driven out.
* Volatile impurities of S, As and P are removed as their volatile oxides.
* Water is removed from hydrated oxide

$$Al_2O_3.\ 2H_2O \xrightarrow[\Delta]{} Al_2O_3 + 2H_2O$$

Bauxite (Alumina)

$$Fe_2O_3.\ 3H_2O \xrightarrow[\Delta]{} Fe_2O_3 + 3H_2O$$

* Carbonates are converted to respective oxide.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$CaCO_3.Mg\,CO_3 \xrightarrow{\Delta} CaO + MgO + 2\,CO_2$$

(Dolomite)

$$CuCO_3.\ Cu(OH)_2 \xrightarrow{\Delta} 2CuO + CO_2 + H_2O$$

Malachite

$$ZnCO_3 \xrightarrow{\Delta} ZnO(s) + CO_2(g)$$

* It makes the ore porous hence easily workble in subsequent stages.

2. **Roasting** : Converting an ore into its metallic oxide heating strongly at a temperature insufficient to melt in excess of air. Carried out in a reverberatory furnance.

Following changes occur during this process ——

* Moisture is removed.
* organic matter is destroyed.
* S, P, As are oxidised and removed as their respective oxide.

$$S_8 + 8O_2 \rightarrow 8SO_2$$

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

$$4As + 3O_2 \rightarrow 2As_2O_3$$

* Ore converted to metal oxide.

e.g. $2\ Zns + 3O_2 \rightarrow 2\,ZnO + 2SO_2 \uparrow$

C. **Smelting :** This is a process of reduction carried out in a blast furance (extraction of iron)

* Flux is dded to remove the impurities as slag.

$$CaO(S) \quad + \quad SiO_2(S) \quad \longrightarrow \quad CaSiO_3(l)$$

(Basic impurity) acidic flux slag

Gangue (impurity) + flux = slag

slag flootes over metal (l). (to be tapped out)

C and CO can act as reducing agent.

$\rightarrow$Coke : $C + O_2 \rightarrow CO_2$

$$CO_2 + C(coke) \longrightarrow 2CO$$

CO redeuces iron oxide

$$FeO + CO \xrightarrow{1123K} Fe + CO_2$$

$$Fe_2O_3 + CO \xrightarrow{823K} 2FeO + CO_2$$

In some cases the metal gets is obtained by **cathodic reduction** on electrolysis as Na metal obtained from molten NaCl and Al metal from alumina and cryolite at 1150-1173 K.

d. **Refining :** The purification is carried out differently for different metals. The process of purifying the Crude metals is called refining. The impurity may contain other metals, nonmetals, ureocted oxides and sulfides, slag, flux etc.

Example

(i) Distillation process : Zn, Hg, Cd etc.

(ii) Liqution process : In sloping heart pure metal(l) descends (m. p. of metal < that of impurity) Sn, Pb

(iii) Oxidation process: Impurities have greater tendency to be oxidised than metal itself. This can be done by

(a) Bessemerisation for refining copper matte.

(b) Cupellation when impure metal contains other metal as impurities. e.g. Pb removed from Ag. Pb escapes as PbO(volatile)

(c) Poling : Crude metal containing its oxide as impurity. Molten crude metal is stirred wood liberating (CH_4) acting as reductant.

$$3Cu_2O \text{ (of blister copper)} + CH_4 \longrightarrow 6\,Cu + 2H_2O + CO$$

(iv) Electrorefining : Cu, Al, (Anode mud may contain less electro positive metals like Au, Ag, Te etc.

(v) Zone refining : Crude metal melt (l) is allowed to Cool, pure metal crystallises but impurity present in solution (melt)./ Si, Ge, Ga are purified by this method.

(vi) Vapour - phase refining :

$$\underset{\text{(Crude)}}{Ni + 4CO} \xrightarrow{330-350K} \underset{\text{leaving the impurities}}{Ni(CO)_{4(g)}} \xrightarrow{450-470K} \underset{\text{(pure)}}{Ni + CO\uparrow}$$

$$Zr_{(s)} + 2I_2 \xrightarrow{870K} ZnI_{4(g)} \xrightarrow{2075K} \underset{\text{(Pure)}}{Zn(s)\uparrow} + 2I_2(g)$$

$$Ti(s) + 2I_2(s) \xrightarrow{523K} TiI_4(g) \xrightarrow{1700K} Ti(s) + 2I_2(g)$$

Thermodynamic principles of metallurgy :

We know — $\Delta G^0 = RT\,In\,K,$ where K is the equilibrium constant of reversible reaction at temperature

(i) Feasibility of the reaction : $\Delta G = -ve$. More is the negative value more is the progress in forward direction yielding better. $\Delta S = +ve, T\Delta S > \Delta H$, as

$$\Delta G = \Delta H - T\Delta S$$

(ii) Coupling of reaction :

For a reaction $\Delta G = +ve,$ it is to be coupled with another reaction of large negative value of ΔG as a result net ΔG is –ve. Such coupling reaction enable to produce product.

$A \rightarrow B \qquad \Delta G_1 = +ve$

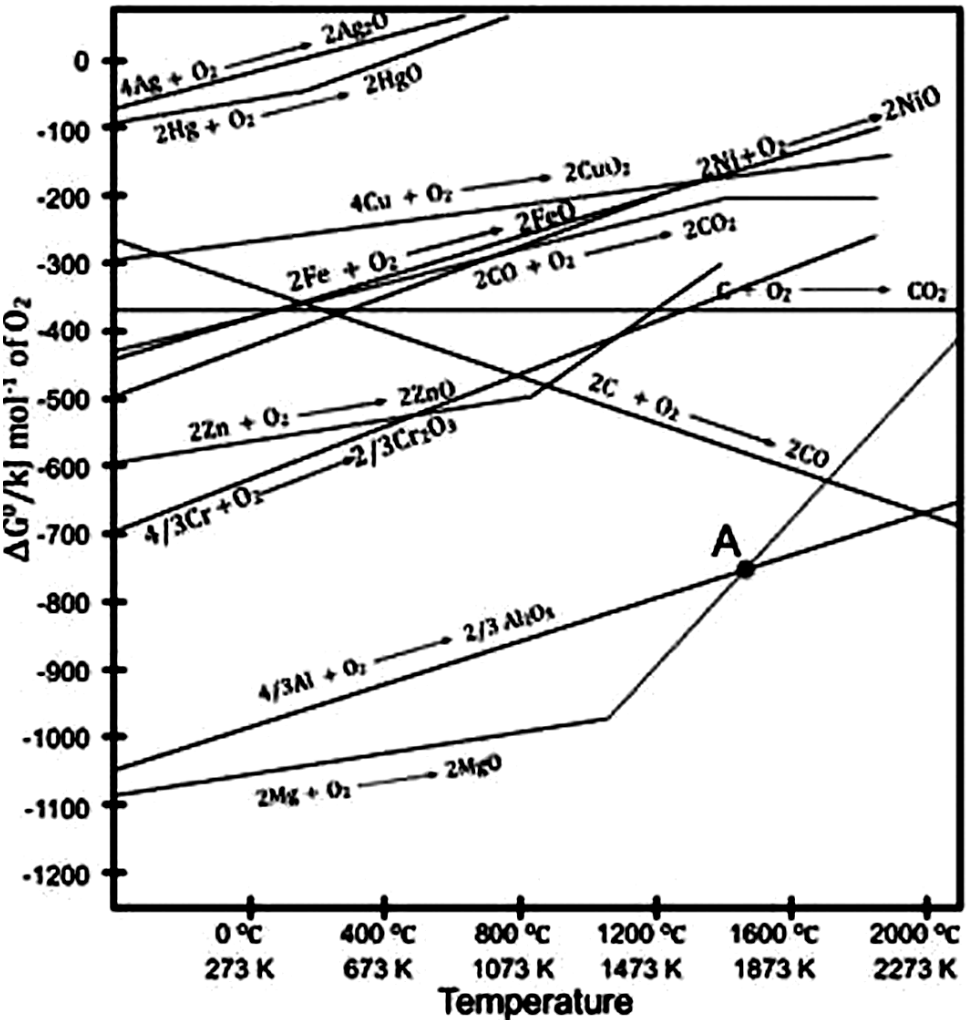
$C \rightarrow D \qquad \Delta G_2 = -ve$

After coupling both the reactions :

$$A + C \longrightarrow B + D,\ \Delta G = \Delta G_1 + \Delta G_2 = -\text{ve}$$

i.e., ΔG_2 (more negative) > ΔG_1

such coupling reactions can easily be understood in terms of Ellingham diagram which plots standard free energy of formation of oxides i.e, $\Delta_f G^0 / \text{mol}$ as a function of absolute temperature (T).



This predicts thermal reduction of an ore $(\Delta G = -\text{ve})$

→ study of the diagram :

Step- I Formation of metal oxide.

Let as have a reaction of the type

$$2xM_{(s)} + O_2 \longrightarrow 2M_xO(s)$$

$\Delta S = -\text{ve}$ (gas to solid)

$T\Delta S$ becomes more –ve.

$\Delta G = \Delta H - T\Delta S$, ΔG becomes less negative.

The graph slows the ΔG becomes less –ve with rise of T-value i.e., $\Delta G - T$ plot has +ve slope.

Step - II When there is a phase change , (i) $S \rightarrow L$ or (ii) $L \rightarrow G$, there is marked charge in the plot (ΔG becomes negative) as ΔS becomes +ve. ΔG decreases (spontaneous).

e.g., Zn – ZnO plot, at the m.p. it is indicated by an abrust charge in the curve.

→ There is a point in a curve below which ΔG is negatiave (more) (MxO is stable) above this point ΔG is less negative reverse reaction, (ΔG = more negative) favours.

$$2M_xO_{(s)} \longrightarrow 2xM_{(s)} + O_2(g)$$

i.e., M_xO will decompose on its own.

At lower temperature metal oxide is stable (ΔS more-ve), at higher temperature metal oxide ΔG, is less negative or positive.

→ The metal easily oxidises i.e., more –ve ΔG acts as better reducing agent. Al reduces FeO, CrO, NiO in thermite reaction but not MgO.

i.e., Al easily oxidises ΔG = more –ve. But Mg can reduce Al_2O_3 (Below the point ‘A’ in the curve)

But this process is not economical.

→ Any metal will reduce the oxide of other metal which lie above it is the diagram.

→ Limitations :

(i) It is silent of rate of reaction.

(ii) ΔG^0 is based upon equilibrium constant, ‘K’, presuming that

$$M_xO + A \text{ (reducing agent)} \rightleftharpoons xM + AO$$

But this is not always true as (oxidant)
reactant and product may be in solid state.

* **Metallurgy of zinc :**

Occurence zinc spar, Zn CO_3, Calamine - Zn CO_3
Zinc blende ZnS, Zincite – ZnO
Willemite - 2 ZnO, SiO_2.
Franklinite - (ZnFe)O. Fe_2O_3 Zinc spinal - ZnO. Al_2O_3

→ **Concentration :**

→ Roasting and calcination

$$2ZnS + 3O_2 \xrightarrow{1173K} 2\,ZnO + 2SO_2$$

$$ZnCO_3 \xrightarrow{\text{Calcination}} ZnO + CO_2$$

→ Reduction of ZnO : As seen in the Ellingham diagram ZnO and C–CO curves intersects at higher temperature bove 1270 K, $C + O_2 \rightarrow CO_2 \rightarrow 2CO$ and $2C+O^2$ remains below Zn – ZnO plot i.e., oxidation of is more spontaneous, hence act as reducing agent.

$$ZnO + C \rightarrow CO + Zn$$

$$2ZnO + C \rightarrow CO_2 + 2Zn$$

ZnO is made into brickettes with Coke and clay & heated at temperature around 1673 K & reduction process goes to completion.

As it’s above the b.p. of Zn, the metal is distilled & collected by rapid chilling.

HOME ASSIGNMENT

(a) Match the following :

Chile saltpeter	$MgCl_2 . KCl . 6H_2O$
Magnesite	ZnO
Carnalite	$NaNO_3$
Malachite	$ZnCO_3$
Zincite	$K_2SO_4 . Al_2(SO_4)_3 .4Al(OH)_3$
Calamine	$Fe_2O_3 . 3H_2O$
Alunite	$Cu(OH)_2 .2\ Cu\ CO_3$
Limonite	Magnesium carbonate.

(b) Fill in the blanks :

(i) Sulfide ore is concentrated by _______.

(ii) In pressure NaCN _____ gets in contact with froth.

(iii) (Wolfram & tinstone) is concentrated by _______

(iv) Alumina from buxite is obtained by the process of ______

(v) If P2O5is the impurity _______ acts as flux.

(c) Explain the following :-

(i) Metal usually don't occur as nitrate.

(ii) All minerals are not ores.

(iii) Cu and Ag have +ve E0 values yet they are found in combined state as sulfide but not as oxide.

(iv) Elements with high atomic number are increasingly rare.

(v) CO is a more effective reducing agent than carbon below 983 K but above this temperature reverse is true.

(d) (i) Predict the purification process for the following crude metal.
Cu, Al, Ge, Zr

(ii) What is anode mud ?

(iii) How can you separate Zn from iron ?

(iv) What is gangue ?

(v) Name the flux used during iron extraction (smelting).

Lecture -34, 35, 36

principle of extraction of Aluminium :

In Elingham diagram 'Al' is much below C. Thus Al_2O_3 is much more stable due more-ve ΔG^0 value & cannnot be reduced by carbon. So it undergoes electrolytic reduction or electrometallurgy of molten salt. Metal is liberated at cathode.

$Al^{3+} + 3e^- \longrightarrow Al$. Here reduction is compared to carbon as Al as Al is coupled with carbon. Al^{3+} has higher reduction potential than C. So C oxidises to CO/CO_2 at anode. $\Delta G^0 = -nFE^0$, the over all ΔG^0 of the coupled reaction becomes –ve.

Metallurgy :

Ores : Bauxite ($Al_2O_3 . 2H_2O$)

Diaspore $(Al_2O_3.H_2O)$

Corundum (Al_2O_3)

Cryolite - $Na_3 AlF_6$

→ Concentration of the ore - Leaching (Bayer's process using NaOH)

→ Electrolyte : melt - concentrated ore + cryolite + fluorspar (CaF_2). Crylite and fluorspar reduces the mp around 1140 K & make it good conductor of electricity.

→ Hall - Heroult electrolytic cell

Cathode - Iron tank lined with carbon

Anode-suspended graphite rods.

Electrode reactions :

Cathode- $Al^{3+}(melt) + 3\overline{e} \longrightarrow Al(l)$

Anode - $C_{(s)} + O^{2-}(melt) \longrightarrow CO + 2r\overline{e}$

$C + 2O^{2-}(melt) \longrightarrow CO_2(g) + 2\overline{e}$

(graphite anode therefore changed from time to time)

The metal obtained by this process is 99.95% pure.

→ At anode, CO_2, F_2, O_2 and carbon compounds of fluorine are formed.

Principle of Extraction of Copper :

Ores : Chalcopyrite , $Cu Fe S_2$

Chaleocite , $Cu_2 S$

Copper also present in native state (99.9% pure) in Michigan (USA).

Principle : In the Ellingham diagram carbon & CO present below Cu-CuO plot. Hence can be reduced by C or CO. in the temperature range of 500-600K. Sulphide ore or Malachite, $CuCO_3 . Cu(OH)_2$, acurite [$2CuCO_3 . Cu(OH)_2$] converted to CuO. The crude metal is refined by electrolytic method.

Flow chart of extraction :

$$\boxed{\text{Chalcopyrite ore}} \xrightarrow[\text{Froth floatation process}]{\text{Concentration}} \boxed{\text{Concentrated ore}} \xrightarrow[\text{reverberatory furnace}]{\text{Roasting in}} \boxed{\begin{array}{c} Cu_2S + FeS \\ \& \\ Cu_2O \end{array}}$$

$$\xrightarrow[\text{roasted ore} + C + SiO_2]{\text{Smelting}} \boxed{\begin{array}{c} FeS \rightarrow FeO + SO_2 \\ FeO + SiO_2 \rightarrow FeSiO_3 \\ (FeS + Cu_2S) - \text{malte (slag)} \end{array}} \xrightarrow[\text{Copper melte from blast furnace + air blast}]{\text{Bessemerisation}}$$

$$\boxed{\begin{array}{l} Cu_2S \xrightarrow{O_2} Cu_2O + SO_2 \\ \quad \text{air blast} \\ 2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2 \\ \quad \text{self oxidation} \end{array}} \xrightarrow[\begin{array}{l} \bullet \text{ Blister opper} - \text{anode} \\ \bullet \text{ Pure copper as cathode} \\ \bullet \text{ Electrolyte} - CuSO_4 (aq) \end{array}]{\text{Clectrolyric refining}} \boxed{\begin{array}{l} \text{At cathode} - Cu^{++} + 2e^{-} - Cu \\ 99.9\% \text{ pure} \end{array}}$$

$$\text{Blister copper(98\% Cu)} \xrightarrow[\text{Reverberatory fumace}]{\text{Poling}} \text{Cu (99.5\%)}$$

From none sulfide ore :

Non sulfide ore :

$\downarrow$ crushed

powdered ore

$\downarrow$ + powdered coke in reverberatory furane

$Cu\ (CuO + C \rightarrow Cu + CO)$

$$\boxed{\begin{array}{l} \text{Malachite ore } CuCO_3.Cu(OH)_2 - \\ \text{basic copper carbonate} \\ \text{Azurite ore } 2\,CuCO_3.Cu(OH)_2 \end{array}}$$

$\downarrow$ dil H_2SO_4 Liached)

$CuSO_4$(aq).

$\downarrow$ Electrolysis

At cathode : $Cu^{2+} + 2\overline{e} \rightarrow$ Cu (Pure)

Extraction of Iron :

Occurrence : Ores are present in form of oxide, carbonate and sulfide.

Oxide ore : Haematite, Fe_2O_3 (red)

Magnetic, Fe_3O_4 (Black)

Limonite, Fe_2O_3. $3H_2O$

Carbonate ore : Siderite or spathic iron - Fe CO_3

Sulfide ore : Iron pyrite, Fe S_2 (For preparation SO_2, H_2S)

Chalcopyrite - $CuFeS_2$ (For extracting of Cu)

Flow chart of extraction :

$$\boxed{\text{Powdered ore}} \xrightarrow[\text{Magnetic separations}]{\text{Gravity separation (washing)}} \boxed{\text{Concentrated ore}} \xrightarrow[\text{roasting with little coke in kilns}]{\text{Calcination \&}}$$

$$\boxed{\begin{array}{l} S_8+8O_2 \rightarrow 8SO_2\uparrow \\ P_4+5O_2 \rightarrow 2P_2O_5\uparrow \\ 4As+5O_2 \rightarrow 2As_2O_5\uparrow \\ 4FeO+O_2 \rightarrow 2Fe_2O_3 \end{array}} \xrightarrow[\substack{\text{(Blast furnace fed with} \\ \text{roasted ore}+CaCO_3+C(\text{coke}))}]{\text{Smelting reduction}} \boxed{\begin{array}{l} Fe_2O_3+3CO \rightarrow 2Fe+3CO_2 \\ 2FeO+C \rightarrow 2Fe+CO_2 \end{array}}$$

Molten iron leaving $CaSiO_3$ (slag)

→ Molten iron tapped below the furnace is solidfied into blocks known as **pigiron**.

→ On sudden cooling given white cast iron, cast iron is converted in wrought (pure form) iron or steel.

Refining: pig iron is converted to steel.

Steel is more useful than iron. steel is sufter and more malleable than pig or castiron. Conversion of pig iron to steel is purification process. This can be processed through any of the following processes.

(a) Bassemer process
(b) Open Heart process
(c) Electric furnace process.

HOME ASSIGNMENT

(a) Fill in the gaps :

(i) Spiegeleisen in used during manufacture of _________.
(ii) Thomas slag is a fertiliser, its chemical name is ______.
(iii) Blue flame in the mouth of bessemer converter contains __________ gas.
(iv) The pure form of iron is _________ iron.
(v) The highest % of C-present in ________ iron.

(b) Answer the following :

(i) Name flux used and slag formed in blast furnace during iron extraction.
(ii) Explain the stability of metal oxide above and below the $\Delta G^0 - T$ plot in the Elingham diagram.
(iii) What is the leaching agent used in Baeyer's process of concentration of bauxcite ore ?
(iv) What are depresants ?
(v) What is meant by collector in froth floatation process.

Lecture - 37-40

UNIT - VII

p-block of elements

Group - 15 - element. [Prictogen]

Elements $_{7}N, _{15}P, _{33}As,\ _{51}Sb,\ _{83}Bi,\ _{115}Me^{*}[Mc-290\,has\,t\,{}^{t}\!/_{2}\,0.8sec]$ (moscovium)

→ Electronic configuration : valence shell ns^{2}sp^3 (n=2 to 7)

Atomic radii (covalent radii) There is considerable increase in atomic radii from N to P. But from As to Bi only a small increase in covalent radius. This discrepany due to introduction of filled d (d^{10}) and hf (14 electrons) which have less shielding effect increasing Z* (ENC) value. Greater is the Z* greater is the force of attraction decreasing the radius as the difference is not remarkble.

→ ΔiH value : Due to half filled (p^3) configuration ΔiH of group-15 is much greater than that of corresponding elements present in the same period of group-14. On moving down the group ΔiH value decreases. The irregularities in the difference of $\Delta_i H$ values can be explained in the light of imperfect shielding effect of d & f electrons.

→ Electronegativity : $N^{(3.0)}$ is the most electronegative element of this group. This value decreases down the group. The difference is not much pronounced for heavier elements.

Trends in chemical properties :

→ **Oxidation states :** The ns^2 np^3 configuration suggest its oxidation states from –3 to +5. Compounds in –3 o.s are Mg_3N, Ca_3N_2, Ca_3P_2, Mg_3Bi_2, Zn_3Sb_2 etc. On moving down the group the $\Delta_i H$ value decreases decreasing the stability of (-3) o.s. Nitrogen has a series of elements with o.s. varying from –3 to +5

e.g. $NH_3^{(-3)}, N_2H_4^{(-2)}, NH_2OH^{(-1)}, N_2(o), N_2O^{+1}, NO^{(+2)}\ N_2O_3(+3),\ N_2O_4^{(+4)}, N_2O_5^{(+5)}$

* Phosphorous disproportionates +5 and –3, N into +5 and +2.

$$4H_3P^{+3}O_3 \xrightarrow[\Delta]{} 3H_3{}^{+5}PO_4 + P^{-3}H_3$$

$$3H\overset{+3}{N}O_2 \longrightarrow H\overset{+5}{N}O_3 + H_2O + 2\overset{+2}{N}O$$

As, Sb and B$_i$ become increasingly stable (+3) with respect to disproportionation, because of inert pair effect.

* Due to absence of d-orbitals 'N' has maximum covalenty four it cann't for NCl_3^- can exhibit covalency beyond four.

PCl_5, $[PF_6]^-$, As F_5, $[A_8F_6]^-$ etc.

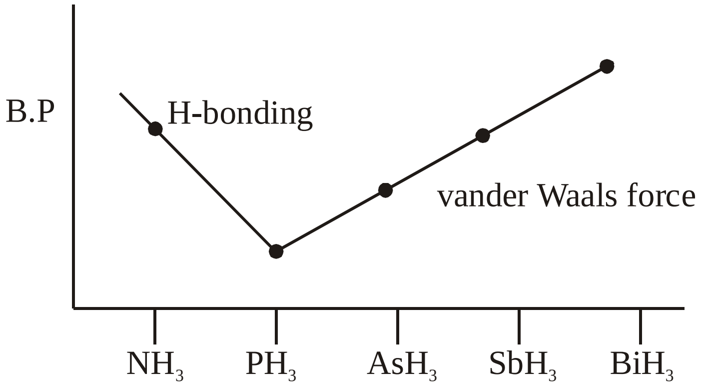
→ **Reaction with hydrogen** General formula. MH_3 these are sp^3 hybridised but pyramidal is shope due to presence of lone pair. *l*-b repulsion compreses the bond angle. The basic character follows in the order

$NH_3 > PH_3 > A_8H_3 > SbH_3 \geq B_iH_3$

* Bond angle : $NH_3\left(107.8^0\right) > PH_3\left(96.6\right) > AsH_3\left(91.8^0\right) > SbH_3(91.3)$

* Boiling point : $NH_3 > PH_3 < AsH_3 < SbH_3 < B.H_3$

$(238.5K \quad 185.5K \quad 210.6K \quad 254.6K \quad 290K$



* Thermal stability : $NH_3 > PH_3 > AsH_3 > SbH_3 < BiH_3$

* Reducing nature : $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

$$BiH_3 \longrightarrow Bi + 3H$$

(Longer B ⟶ H bond on moving down the group)

* Solubility in water : NH_3 completely soluble in water due to formation of inter-molecular H-bonding. other hydrides are insoluble.

→ Reaction with halogen :

(a) Trihalide : All elements of this family form tri-halide Trihalide of Nitrogen except NF_3 are unstable. These are hydrolysed easily

$$NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl$$

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + HCl$$

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl$$

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

Ionic character of trihalide increases on moving down the group.

(b) Penta halide : Due to absence of d-orbital 'N' fails to form pentahalide. In higher oxidation state the compounds are predominately covalent. B_i fails to form penta halide due to inert pair effect.

.→ Reaction with oxygen : These element can form oxides of the type M_2O_3 and M_2O_5. N_2O_3, P_2O_3 & As_2O_3 are acidic, the acidic character decreases down the group. Sb_2O_3 is amphoteric while B_2iO_3 is basic. Nitrogen form a series of oxides, N_2O, NO, NO_2, N_2O_3, N_2O_4, N_2O_5. Among these N_2O_5 is the strongest acidic oxide, Bi_2O_3 is the weakest.

→ Formation of oxyacids :

All can form oxy acids, –ous, -ic acids etc.

e.g., HNO_2, HNO_3 ; H_3PO_3, H_3PO_4 etc.

Anomalous behaviour of Nitrogen

(i) Small size and high electronegativity value.

(ii) Physical state : N_2(gas) but other are solids.
Nitrogen is diatomic but phosphorus is tetra-atomic (P_4).

(iii) Non-availability d-orbitals. ${}_7N = 1s^2\ 2s^2\ 2p^3$.

(a) Covalency state maximises to 4 $\left(\overset{+}{N}H_4\right)$

(b) Ability to form $p_\pi d_\pi$, bond other members can form $d_\pi - p_\pi$ bond $R_3P{=}CH_2$

(iv) Due to small size N can form multiple bonds with itself and with other elements having small size & greater electronegativity e.g. CN, NO .... etc.

((v) Due to weaker N–N bond it fails to catenate.

DINITROGEN (N_2)

(i) $$\begin{array}{c} NH_4Cl(aq) + NaNO_2(aq) \longrightarrow NH_4NO_2 \xrightarrow[\Delta]{} N_2(g) + 2H_2O(\ell) \\ + \\ NaCl \end{array}$$

(ii) $$\left(NH_4\right)_2 Cr_2 O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$$

(iii) $$2NaN_3 \xrightarrow{\Delta} 2Na + 3N_2$$

$$Ba\left(N_3\right)_2 \xrightarrow{\Delta} Ba + 3N_2$$

(iv) Commercial method : Fractional distillation air (ℓ) where $N_2(\ell)$ collected at 77.2 K

Properties :

Due presence of triple $(N \equiv N)$ and high ΔaH (941.4 kJ mol^{-1}) it's treated as an inactive gas. But under high temperature & pressure it reacts to form different compounds.

$$N_2 + \left|\begin{array}{l} \xrightarrow[\Delta]{Li(s)} Li_3N \\ \xrightarrow[\Delta]{Mg(s)} Mg_3N_2 \qquad \xrightarrow{H_2O} Mg(OH)_3 + NH_3 \\ \xrightarrow[773K-200atm]{H_2(g)} NH_3 \\ \xrightarrow[2000K]{O_2(g)} NO \\ \xrightarrow[1273K]{CaC_2(s)} CaCN_2 \xrightarrow{H_2O} NH_3(g) + CaCO_3 \end{array}\right.$$

(Calcium cyanamide)

($CaCN_2$+C) is called nitrolim used as fertiliser.

Uses :(i) Manufacture of NH_3, HNO_3, $CaCN_2$ etc.

(ii) To create inert atmosphere

(iii) $N_2(\ell)$ used as refrigerant

Ammonia

(a) Synthesis (Haber's process)

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 93.6\,kJ$$

Conditions for better yield : (Lechatelier's principle)

(i) Hign concn. of pure & dry N_2 & H_2.

(ii) As exothermic an optimum temperature of 500^0C is applied just to facilitate the reaction.

(iii) As Δn is negative high pressusre of 200–900 atm.

(iv) Catalyst - finely divided iron, promotor - M_O.

(b) Lab. method :

$$2NH_4Cl + CaO \xrightarrow{\Delta} CaCl_2 + 2NH_3 \uparrow + H_2O$$

* Dried up by passing through CaO tower.

* Collection - By downward displacement of air can be collected over mercuty.

$$NH_3 + \left| \begin{array}{ll} \xrightarrow{H_2O} & NH_4OH \\ \xrightarrow{HCl} & NH_4Cl \text{ (White fumes)} \\ \xrightarrow[\text{Oxident}]{CuO} & Cu + N_2 + H_2O \\ \xrightarrow[pt]{O_2} & NO + H_2O \\ \xrightarrow{Cl_2} & N_2 + HCl \\ \xrightarrow{Cl_2\,(Excess)} & NCl_3 + HCl(+NH_3 \longrightarrow NH_4Cl) \\ & NI_3 \text{ is used as an explosive.} \\ \xrightarrow{Na} & NaNH_2 \text{ (sodamide)} \\ \xrightarrow{FeCl_3(aq)} & Fe(OH)_3 \\ & \text{(Brown)} \\ \xrightarrow{ZnCl_2} & Zn(OH)_2 \\ \xrightarrow{AgCl(s)} & [Ag(NH_3)_2]Cl \\ & \quad \text{Soluble} \\ \xrightarrow{CuSO_4\,(blue)} & [Cu(CH_3)_4]SO_4 \\ & \text{deep – blue} \\ \xrightarrow[\text{(Nesslerspeagenl)}]{K_2HgI_4 + KOH} & H_2N-Hg-O-Hg-I + KI + H_2O \\ & \text{Iodide of Millon's base (Brown ppt)} \end{array} \right.$$

Uses (a) Synthesis of $(NH_4)_2SO_4$, NH_4NO_3, $(NH_4)_3PO_4$, urea (fertilizer)

(b) synthesis HNO_3 (Ostwald process)

(c) Refigerant

Synthesis of HNO_3 (Ostwald process)

(a) Principle :

$$4NH_3 + 5(O_2) \xrightarrow{pt} 4NO + 6H_2O + 21.5\,K\,cal.$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

→ The impure acid is yellow due to dissolved $NO_2(g)$

→ Acidic properties : (Base + acid $\longrightarrow$ salt + water)

$$CuO + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$$

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

$$Na_2CO_3 + 2HNO_3 \longrightarrow 2NaNO_3 + H_2O + CO_2$$

→ As an oxident : It reduced to different forms like NO, NO_2, NH_4^+ depending on the concentration of HNO_3.

As an oxidant in the reduced form it can be written as ——

$$4H^+ + NO_3^- + 3\bar{e} \longrightarrow NO + 2H_2O$$

$$2H^+ + NO_3^- + \bar{e} \longrightarrow NO_2 + H_2O$$

Cold and dilute → $NO_3^- + 10H^+ + 8e^- \longrightarrow \overset{+}{N}H_4 + 3H_2O$

(i) With H_2S, colloidal 'S' separates.

$$H_2S \longrightarrow S + 2H^+ + 2e^-$$

(ii) With KI – $2I^- \longrightarrow I_2 + 2e^-$

(liberate violet fumes)

(iii) C in aqueous medium converts to CO_3^{2-}.

$$C + 3H_2O \rightarrow CO_3^{2-} + 6H^+ + 4e^-$$

(iv) Conc. HNO_3 helps to oxidise P to PO_4^{3-}, 'S' to SO_4^{2-}

$$As \longrightarrow AsO_4^{3-},\ I_2 \longrightarrow IO_3^-$$

$$4H_2O + P \longrightarrow PO_4^{3-} + 8H^+ + 5e^-$$

With metal

(v) Cold dilute nitric acid with Fe forms ferrous nitrate.

$$Fe \longrightarrow Fe^{2+} + 2e$$

$$Cu \longrightarrow Cu^{2+} + 2e$$

e.g. $NO_3^- + 10H^+ + 8e^- \longrightarrow NH_4^+ + 3H_2O$

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

→ Fe becomes passive with very conc. HNO_3 due to surface oxidation.

→ During brown ring test (test for NO_3^-) the compound formed is ; $\left[Fe(H_2O)_5\ N\overset{+}{O}\right]$,

Penta aqua nitroso Iron(I) sulfate.
(Brown)

Uses : (a) Preparation of aquaregia. $(HNO_3 \text{ and } HCl, 1:3)$ which dissolved Au and Pt.

$$HNO_3 + 3HCl \longrightarrow 2H_2O + NOCl + 2Cl.$$

$$Au + 3Cl \rightarrow AuCl_3$$

$$AuCl_3 + HCl \rightarrow H[AuCl_4]$$

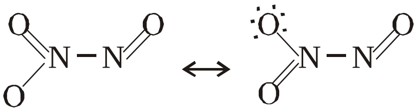
(b) Laboratory reagent.
(c) In the preparation of TNT, picric acid, nitroglycerine.
(d) Purification of gold and silver.

Oxides of Nitrogen : (Structure)

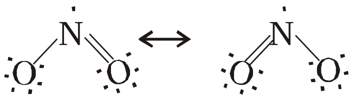
(i) Dinitrogen oxide, N_2O $\quad N = N = O \longleftrightarrow N \equiv N - O$

(ii) Nitrogen (II) oxide, NO $\quad :\dot{N}:=\ddot{O}:\longleftrightarrow :\dot{N}=:\ddot{O}:$

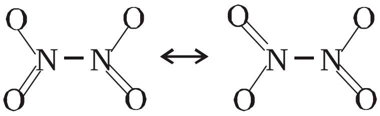
(iii) NItrogen (III) oxide, N_2O_3



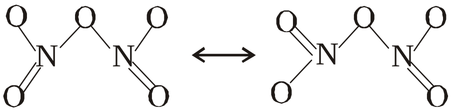
(iv) Nitrogen (IV) oxide NO_2



Nitrogen (IV) oxide N_2O_4



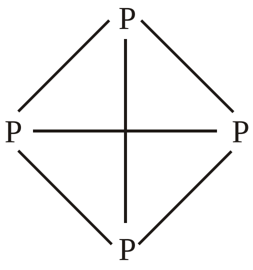
Dinitrogen pentoxide N_2O_5



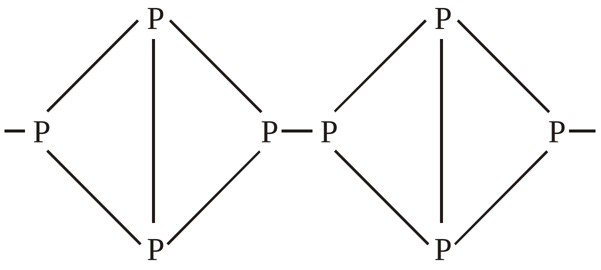
Phosphorus

Allotropes of 'P' = white, red and black

Red phosphorous is more stable than white phosphorus due to polymeric structure.



(White)



Black phosphorus $(\alpha = \text{black})$

$$P(\text{red}) \xrightarrow{803K} \alpha - \text{black 'P'}.$$

It does not conduct electricity, does not form oxide.

$\beta - \text{black}$ white $P \xrightarrow[\text{High pressure}]{473K} \beta - \text{black}$

It is the most stable allotrope of Phosphorus, Highly polymerised with Black metallic structure with layers of graphite like structure & is good conductor of electricity.

Phospine

$P_4 + 3NaOH + 3H_2O \longrightarrow 3\,Na\,H_2PO_2 + PH_3$

Write 'P' Sodium hypophosphite

(P disproportionates)

$$PH_3 \left| \begin{array}{l} \xrightarrow{O_2} P_2O_5 + H_2O \\ \xrightarrow{Cl_2} PCl_3 + HCl \\ \xrightarrow{HI} PH_4I\,(\text{Phosphonium iodie}) \\ \xrightarrow{AgNO_3} Ag_3P\ (\text{Black}) \\ \xrightarrow{N_2O} P_2O_5 + N_2 + H_2O \\ \xrightarrow{CuSO_4} Cu_3P_2 + H_2SO_4 \end{array} \right.$$

Uses : Holme's signal (signalling the presence of ship during right. [Ca_3P_2 & Ca C_2]

- For naval war fare locating enemy position on sea.

Phosphorus halide

$$P_4(s) + 6Cl_2(g) \longrightarrow 5PCl_3(\ell),\ \text{colourless liquid.}$$

$$P_4(s) + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2(g) + 2S_2Cl_2$$

It fumes in moist air due to hydrolysis.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

$$3ROH + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

→ $PCl_5 : P_4(s) + 10Cl_2 \longrightarrow 4PCl_5(s),$ yellowish white (s)

→ PCl_5 exists as ionic solid, $[PCl_4]^+[PCl_6]^-$

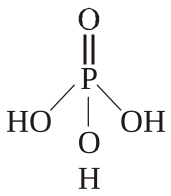
→ –OH group of alcohal and carboxylic acid convert into alkyl halide and acid-chloride.

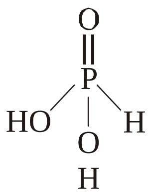
$$RCOOH + PCl_5 \longrightarrow R\,COCl + POCl_3 + HCl$$

Oxo acids of Phosphorus

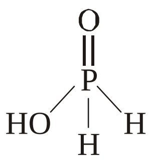
P – O – H forms ionisable H^+ while P–H helps in reduction not in acidic nature.

e.g. H_3PO_4 is tribasic acid while H_3PO_3 is dibasic.

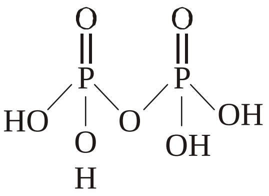




H_3PO_2 is monobasic.



$H_4P_2O_7$, pyrophosphoric acid is tetrabatic
i.e., having four - O–H bonds.



HOME ASSIGNMEBT

1. (a) Nitrolim is mixture of ________ & __________ .
   (b) It is used as ____________ .
   (c) On oxidation of NH_3 __________ acts as catalyst.
   (d) The formula of Nessler's reagent is ________.
   (e) NH_3 is collected by _______ in the laboratory.
2. How can you distinguish between ammonia and PH_3 ?
3. Discuss the properties of hybrides of group-15.
4. What is brown ring test ? What is O.N. of Fe, during the formation of iron complex.
5. Discuss the principles of better yield of ammonia.

Lecture 41 to 44

Group - 16

(CHALCOGENS)

Elements of their electronic configuration :

$_8$O, $_{16}$S, $_{34}$Se, $_{52}$Te, $_{84}$ P_O^* $_{116}$Lv (Livermorium) produced in the Laboratory.

Atomic radius : The size increases from O to P_O with increase of shell number.

Electro-vity : Oxygen is the most electronegative element i.e, = 3.5. The value decreases in mooving down the group with increase of atomic size.

$\Delta_i H$, ionisation enthalpy decreases down the group.

Physical state Oxygen is a diatomic gas, S, Se, Te exists as a octa atomic, $^*P_0$ is a radioactive meta with very shot, half life period.

Oxidatrastate : $O=2s^22p^4$, due to absence of d-orbital, Oxygen has predominately–2 o.s. Oxygen also can exhibit + 1 and +2 o.s. O_2F_2 and OF_2. Other element can have wide variation.

o.s. i.e –2 to +6. Stability of +6 o.s. decreases down the group while that of +4 state increases due to **inert pair of effect.** Both in +4 and +6 covalent bonds are formed.

→ **Reaction with hydrogen :** All form hydrides of formula H_2E (E=element)

(i) **Structure**. All molecules are sp^3 hybridised & of AB_2L_2 (type)

These are bent however the bond angle decreases with decrease of electronegativity. Bond angle of $H_2O = 104.5^0$ $H_2S = 92.1$

(ii) **Boiling point** $H_2O(l) > H_2T_2 > H_2Se > H_2S$. Water has exceptionally high b.p due to inter molecular H-bonding. B.P. first decreases from H_2O to H_2S then rises due to increase size and vander waals force of attraction.

Volatility follows in the order.

$$H_2S > H_2Se > H_2Te > H_2O(\ell)$$

(iii) **Acidic nature :**

$H_2Te > H_2Se > H_2S > H_2O$. This is due to H–E bond length. Thus the Ka value increases down the group.

$$Ka(H_2O) = 1\times10^{-14}, \; Ka(H_2S) = 1.3\times10^{-4}$$

(iv) Thermal stability : decreases down the group with increase of bond length.

$$H_2O > H_2S > H_2Se > H_2Te$$

(v) Reducing nature: Except H_2O all are better reducing agent, as these can give H. With increase of H–E bond length.

$$H_2Te > H_2Se > H_2S$$

$$H_2Te = Te + 2H$$

Oxygen forms another hydride except water i.e. H_2O_2

→ **Reaction with oxygen :** Element of this group form oxides of formula EO_2 and EO_3 with +4 and +6 o.s. Trioxides are more acidic than dioxide.

→ **Reaction with halogen :** The halides in O.S. + 1 (O_2F_2), +2 (OF_2, SF_2...), +4 (SF_4, $POCl_4$.), +6 [SF_6, SeF_6, TeF_6] the stability of these halids follows in the order

$$F^- > Cl^- > Br^- > I^-$$

Formation of oxy acids S, Se and Te form similar oxyacids. These are formed by the reaction of dioxide or trioxide with water.

$$H_2SO_3 \;\; H_2SeO_3 \;\; H_2TeO_3$$

$$H_2SO_4 \;\; H_2SeO_4 \;\; H_2TeO_4$$

i.e., acids with +6 O.S. is more acidic then-ous acids with +4 O.S.

→ **Anomalous behaviour of oxygen ($1s^2\ 2s^2\ 2p^4$)**

Oxygen differs from other elements of the group due to

(i) Its smaller size & high electronegativity value (3.5)

(ii) Non availability of d-orbitals.

Distinguish properties :

(i) H_2O is liquid but other hydrides are gases.

(ii) It resticts its O.S. (–1, –2, –1/2, +1, +2) but others can extend upto +6.

→ **DIOXYGEN**

(i) (a) Thermal decomposition f(a)KClO, $KMnO_4$ and KNO_3.

$$2KMnO_{4(S)} \rightarrow K_2MnO_{4(S)} + MnO_2 + O_{2(g)}$$

(b) Oxides of heavy metals : (HgO, Ag_2O, Pb_3O_4 ....

$2P_3O_4 \rightarrow 6PbO + O_2$

(c) From H_2O_2

$$H_2O_2(aq) \xrightarrow{MnO_2(s)/Ni} H_2O + \frac{1}{2}O_2 \uparrow$$

(d) Electrolysis of acidulated water : dioxygen at anode.

(ii) **Commercial preparation :** Fractional distillation of liquid air (except CO_2 & H_2O(vap). N_2(l) is separated at 77 K while O_2 at (90 K)

→ Metals (except noble metal gold & Pt) directly combine with oxygen to form respective oxide.

$$2Na(s) + O_{2(g)} \xrightarrow{575K} Na_2O_2(s)$$

→ Non-metals (except noble gases) produce corresponding oxide.

$$P_4 + 5O_2 \xrightarrow{\Delta} 2\,P_2O_5$$

→ with certain compounds:

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_3$$

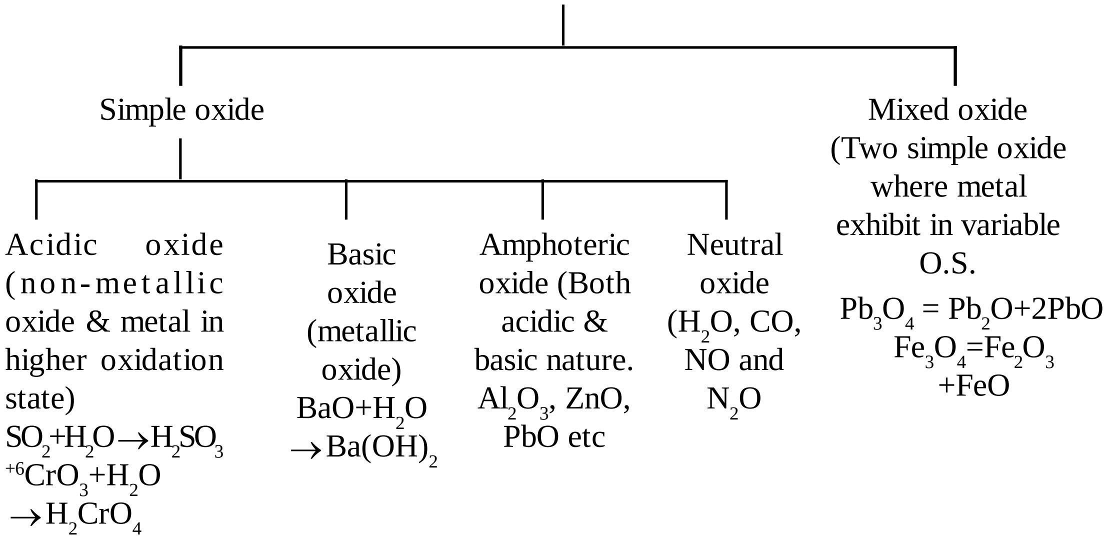
$$4HCl_{(g)} + O_{2(g)} \xrightarrow[700K]{CaCl_2} 2H_2O_{(g)} + Cl_{2(g)}$$

Uses (i) Essential component for **respiration** and **combustion**.

(ii) Liquid O_2 with hydrazine used as rocket fuel.

(iii) Used in Oxy-acetylene torch for cutting & welding.

Classification of oxides



- Simple oxide
  - Acidic oxide (non-metallic oxide & metal in higher oxidation state) $SO_2 + H_2O \rightarrow H_2SO_3$ $^{+6}CrO_3 + H_2O \rightarrow H_2CrO_4$
  - Basic oxide (metallic oxide) $BaO + H_2O \rightarrow Ba(OH)_2$
  - Amphoteric oxide (Both acidic & basic nature. Al_2O_3, ZnO, PbO etc
  - Neutral oxide (H_2O, CO, NO and N_2O
- Mixed oxide (Two simple oxide where metal exhibit in variable O.S. $Pb_3O_4 = Pb_2O + 2PbO$ $Fe_3O_4 = Fe_2O_3 + FeO$

Ozone (O_3)

Principle of preparation :

$3O_2 \underset{\text{discharge}}{\overset{\text{Silent electric}}{\rightleftharpoons}} 2O_3 \quad \Delta H = +142\,kJ/mol$ O_3 is unstable at ordinary temperature, should be removed from the reaction medium to avoid decomposition. Low temperature is maintained to avoid decomposition.

The **instrument** used for the purpose is called ozoniser.

(i) Siemen's ozoniser (10% O_2 converted to O_3) (ii) Brodie's ozoniser.

(25% O_2 by weight converted to ozone)

Draw and explain the diagram.

Purification :

Ozonised oxygen (O_2+O_3) $\xrightarrow{\text{liquid air}}$ Condensed to deep blue (ℓ)

↓ Fractional evaporation

O_2 at 90 K | less volatile ozone at 161.1 K

Stability : $O_3 \rightarrow O_2 + O$

$\Delta H = +ve$ and $\Delta S = +ve$

$\Delta G = \Delta H - T\Delta S$

Increase of ΔS can be made so that ΔG negative. That is why high concentration of Ozone is dangerously explosive. The reaction proceeds towards right making $T\Delta S > \Delta H$ (at a given temperature) as ΔS increases with high concentration O_3.

→ Ozone as Oxidant : $O_3 \rightarrow O_2 + O$

(acidic medium) $O_3 + 2H^+ + O_2 + H_2O$

(alkaline medium) $O_3 + H_2O + 2\overline{e} \longrightarrow O_2 + 2(OH)^-$

$O_3 + 6H^+ + 6e^- \longrightarrow 3H_2O$

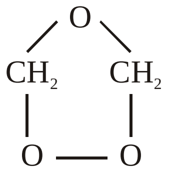
$\underline{Sn^{2+} \longrightarrow Sn^{4+} + 2e^-}$

→ Reducing agent : Reduces peroxides (H_2O_2, Ba O_2) liberating oxygen.

$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$

$BaO_2 + O_3 \longrightarrow BaO + 2O_2$

→ Formation of ozonide. $CH_2 = CH_2 + O_3 \longrightarrow$



Bleaching agent : $O_3 \rightarrow O_2 + O$

Coloured matter $\xrightarrow{+[O]}$ Bleached.

Depletion of ozone layer.

NO (Supersonic jet etc) + $O_3 \rightarrow NO_2(g) + O_2$

Ozone (O_3) –

$\xrightarrow{\Delta} O_2$

$\xrightarrow{Hg, Ag} HgO, AgO$

$\xrightarrow{KI} I_2$

$\xrightarrow{HCl} Cl_2$

$\xrightarrow{SO_2} SO_3$ $(SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-$

$\xrightarrow{SnCl_4} SnCl_4$

$\xrightarrow{K_4[Fe(CN)_6]} K_3[Fe(CN)_6]$

$\xrightarrow{FeSO_4} Fe_2(SO_4)_3$

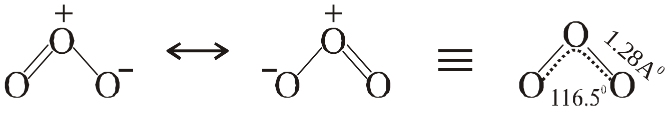
$\xrightarrow{I_2} HIO_3$ $I_2 + 6H_2O \longrightarrow 2IO_3^- + 12H^+ + 10e^-$

$\xrightarrow{K_2MnO_4} KMnO_4,$ $MnO_4^{2-} \longrightarrow MnO_4^- + e^-$

Uses (a) As a germicide it's used to sterilise drinking water.

(b) Purifying air in crowded places , underground railways.

Structure of ozone (Oxygen is paramagnetic but ozone is not)



SULFURDIOXIDE (SO_2)

$$Cu + (Conc.)\,2H_2SO_4 \xrightarrow{\Delta} CuSO_4 + 2H_2O + SO_2 \uparrow$$

Purification : dried by passing through conc. H_2SO_4.

Collection : Upwards displacement of air.

It is a colourless gas with burning sulfur smell.

→ It is acidic in nature . Moist blue litmus turns red.

$$SO_2 + H_2O \rightarrow H_2SO_3 \text{ (Sulfurous acid)}$$

→ Reducing agent :

$$SO_2 + H_2O \rightarrow SO_3 + 2(H)$$

$$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$$

e.g. It reduces ferric sulfate to ferrous sulfate.

$$\begin{array}{c} 2Fe^{3+} + 2e \longrightarrow 2Fe^{2+} \\ \hline SO_2 + 2H_2O + 2Fe^{3+} \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+ \end{array}$$

→ Bleaching action:

$$SO_2 + H_2O \rightarrow SO_3 + 2(H)$$

$$\begin{tikzcd} \text{Coloured matter} + [H] \arrow[r] & \text{Bleached} \arrow[l, bend left, "\text{air}\,(O_2)"] \end{tikzcd}$$

Bleached matter may regain its colour due to aerial oxidation. Hence bleaching by SO_2 is temporary.

$$SO_2 \xrightarrow{CaO} CaSO_3$$

$$SO_2 \xrightarrow{\text{lime water}} \underset{\text{milkiness}}{CaSO_3} \xrightarrow{SO_2} \underset{\text{milkiness disappears}}{Ca(HSO_3)_2}$$

$$SO_2 \xrightarrow{KMnO_4} MnSO_4 \text{ (Colour fades)}$$

$$SO_2 \xrightarrow[+H^+]{K_2Cr_2O_7 \text{ (Orange)}} Cr_2(SO_4)_3, \text{green}$$

$$SO_2 \xrightarrow{X_2} HX$$

$$SO_2 \xrightarrow{IO_3^-} I_2,\ 2H^+ + 2IO_3^- + 10e^- \longrightarrow I_2 + 6H_2O$$

$$SO_2 \xrightarrow{H_2S} S$$

$$SO_2 \xrightarrow{HI} I_2$$

$$SO_2 \xrightarrow{Cl_2} SO_2Cl_2 \text{ (sulfuryl chloride)}$$

$$SO_2 \xrightarrow{O_2} SO_3$$

$$SO_2 \xrightarrow{\text{Peroxide}} SO_4^{2-}$$

Uses : (i) In the manufacture of sulfuric acid

(ii) As antichlor in the fabric, textile inductry

MANUFACTURE OF SULFURIC ACID

Materials required by contact process

(i) Sulfur dioxide
(ii) air
(iii) Plantised asbestos / finely divided plantinum / V_2O_5

$$2SO_2 + O_2 \overset{V_2O_5}{\rightleftharpoons} 2SO_3 \quad \Delta H = -45.2\,K\,cal$$

Carditras as per Le-chatelier's principle :

(i) Excess of O_2 or air
(ii) high pressure (1.5-1.7 atm.)
(iii) low temperature (optimum temperature of 450-500^{0}C)
(iv) $SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$ (oleum)

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

It (SO_3) was not absorbed in water due to

(i) The reaction is exothermic (ii) forth formation hinders mixing.

H_2SO_4 + Metal/ metal oxide / metal hydroxide/ metal carbonate $\longrightarrow$ respective salt

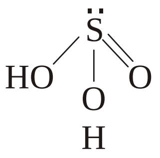
$$H_2SO_4 \left| \begin{array}{l} \xrightarrow{\text{Carbon}} CO_2 \\ \xrightarrow{S} SO_2 \\ \xrightarrow{H_2S} S \\ \xrightarrow{KI} I_2 \\ \xrightarrow[(X=Br,I)]{HX} X_2 + SO_2 \\ \xrightarrow[\Delta]{Cu} SO_2 \\ \xrightarrow{\text{Sugar}} C + H_2O \\ \qquad \text{Sugar charcoal} \\ \xrightarrow{\text{Benzene}} \text{Benzene sulfonic acid} \\ \xrightarrow{NaCl} HCl \\ \xrightarrow{KNO_3} HNO_3 \\ \xrightarrow{SO_3} H_2S_2O_7 \\ \xrightarrow[\Delta]{} SO_2 + H_2O + O_2 \\ \xrightarrow{NaNO_2} \text{HONO (nitrous acid)} \end{array} \right.$$

- $SO_4^{=} + 4H^{-} + 2e^{-} \longrightarrow SO_2 + 2H_2O$

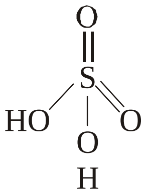
$$\underline{H_2S \longrightarrow S + 2H^{+} + 2e^{-}}$$

Structure of oxoacids of sulfur

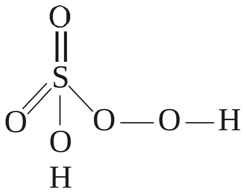
H_2SO_3 sulfurous acid



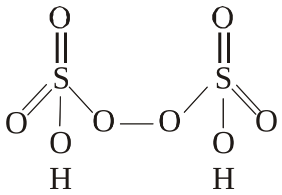
H_2SO_4 Sulfuric acid



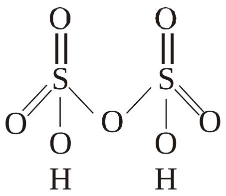
Peroxomonosulfuric acid (Caro's acid)



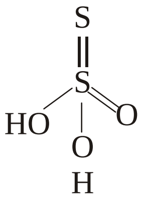
Peroxodisulfuric acid



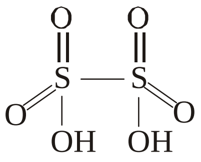
Pyrosulfuric acid (oleum)



Thiosulfuric acid ($H_2S_2O_3$)



Dithionic acid ($H_2S_2O_6$)



HOME ASSIGNMENT

1. (a) Name the metal that continues to burn in the atmosphere of SO_2.
   (b) The bond angle of SO_2 molecule is ________.
   (c) The shape and hybridisation in case of 'S' in SO_2 are _____ & ______.
   (d) Antichlore is the other name of _________.
   (e) What is oleum ?
2. **Explain the following :** s
   (a) Concentrated sulfuric acid is a syrupy liquid.
   (b) O_2 is a gas but sulpur is a solid.
   (c) H_2O is liquid but H_2S is a gas.
   (d) H_2S in more acidic than H_2O.
   (e) SO_2(g) turns potassium dichromate solution green.

Lecture - 45-49

Group 17 elements

GENERAL CHARACTERISTICS OF ELEMENTS OF HALOGEN FAMILY

Fluorine ($_9F$), Chlorine ($_{17}Cl$), Bromine ($_{35}Br$), Iodine ($_{53}I$) and Astatine ($_{85}At$) and Ts 117Ts = synthetic element (Tennessine) discovered in 2010 are me members of halogen family of Group VIIA or Group 17. The word '**halogen**' is derived from two Greek words, '**halos**' means '**sea salt**' and '**genes**' means 'produce'. These elements are called halogens, because these are produced from sea salts, like NaCl, KBr, KI etc. The general characteristic properties of these elements are briefly discussed as follows:

(i) Electronic Configuration: valence shell ns^2 np^5 n = 2 to 7

(ii) **Atomic and Ionic radii:** These elements of halogen family have the smallest size in their respective periods.

Atomic and ionic radii of these elements increase from top to bottom due to successive addition of new shells.

(iii) **Density:** The density of these elements, regularly increases down the group.

(iv) **Electropositive nature:** Electropositive nature gradually increases from fluorine to astatine on moving down the group.

(v) **Melting point and Boiling point:** The melting point and boiling point of members of halogen family increase on going down the group from fluorine to astatine.

(vi) **Ionisation Energy :** $(\Delta_i H)$ these elements of halogen family have very high ionisation energy due to their small size. These elements have the second highest ionisation energy (next to elements of zero group) in their respective periods. Ionisation energy of these elements gradually decreases from top to bottom due to increase of atomic radii on moving down the group.

(vii) Electron gain enthalpy $(\Delta_{eg} H)$:

The energy released on addition of e^- to an isolated gaseous atom. $x_{(g)} + e^- \rightarrow x^-_{(g)} + \text{energy}$ more negative the value more is the affinity. Affinity is qualitative while $\Delta_{eg}H$ is quantitative. $\Delta_{eg}H$ values follow in the order.

Fluorine < Chlorine > Bromine > Iodine > Astatine.

Exceptionally fluorine has less electron affinity than chlorine due to its very small and compact size, where the inter electronic repulsion is relatively more as compared to that in chlorine atom. which has seven electrons in the larger sized M-shell.

$$F_{(g)} + e \longrightarrow F^- + \phi_1. \qquad \phi_2 > \phi_1$$

$$Cl + e^- \rightarrow Cl^- + \phi_2$$

(viii) **Electronegativity :** These elements have the highest electronegativity among all other elements in their respective periods. Fluorine has the highest electronegativity in this group, which gradually decreases down the group in the order :

F	>	Cl	>	Br	>	I	>	At
(4.0)		(3.0)		(2.8)		(2.5)		(2.2)

(ix) **Conductivity:** Due to non-metallic character, all these elements are poor conductor of heat and electricity.

(x) **Molecular state:** Halogens remain in diatomic state and hence are generally represented as X_2 (= F_2, Cl_2 Br_2 and I_2).

(xi) **Physical state:** Fluorine and chlorine are gases, bromine is a reddish brown fuming liquid, while iodine is violet solid at room temperature. The change of state is due to the increase of van der Waals' force of attraction.

(xii) **Colour in gaseous state:** Colour of halogens in gaseous state gradually **intensified** from fluorine to iodine. Low frequency absorbed as the size increases from top to bottom, the complementary colour is observed.

e.g . :

Fluorine (F_2)	Pale yellow
Chlorine (Cl_2)	Greenish yellow
Bromine (Br_2)	Reddish brown
Iodine (I_2)	Deep violet

(xiii) **Valency and Oxidation states:** All these elements show univalency i.e. - 1 or + 1 oxidation state due to shortage of one electron to attain octet state, as they have seven electrons in the valency shell. Fluorine being the most electronegative element shows only - 1 oxidation state. In different excited states chlorine, bromine and iodine show + 3, + 5 and + 7 oxidation states due to availability vacant outer d-orbitals.

(xiv) **Oxidising nature:** Due to their strong tendency to gain an electron, halogens act as strong oxidising agents. The oxidising power decreases on moving down the group. This can be viewed from its reduction potential values. More positive is the reduction potential better an oxident.

$$E_{\frac{1}{2}F_2 \,|\, F^-_{aq}} = 2.87\,\text{volt}$$

i.e., Fluorine is the must powerful oxidising agent.

(xv) **Hydride formation :**

(a) All the halogens react with H_2 to form their respective hydrides, such as HF, HC*l*, HBr, HI.

(b) The decreasing order of Bond energy is HF > HCl >HBr >HI.

(c) The decreasing order of acidic strength is HI > HBr > HCl > HF.

(d) The decreasing order of Reducing nature is HI > HBr > HC*l* > HF.

(e) The decreasing order of covalent nature is HI > HBr > HCl > HF.

(f) The decreasing order of thermal stability is HF>HCl>HBr>HI.

(g) HF is a low boiling liquid. The liquid state is due to strong intermolecular H-bonding. HC*l*, HBr and HI are gases.

(xvi) **Oxide formation:**

(a) F_2 forms two oxides F_2O and F_2O_2 which are called oxygen flourides. The other halogens form their respective oxides.

(b) Cl, Br & I oxides can exhibit + 1 to +7 oxidation state but flourine only shows '- 1' oxidation state.

(c) These oxides are covalent in nature due to less electronegativity difference between oxygen and halogen.

(d) These oxides are strong oxidising agents.

(e) The acidic nature increases with the increase of oxidation state.

(xvii) **With alkali metals:** Halogens react with alkali metals to form corresponding salts. These salts are electrovalent compounds of the type MX, such as NaF, KF, NaC*l*, KCZ, KBr, KI etc.

$$2Na + Cl_2 \longrightarrow 2NaCl$$

(xviii) **Oxoacids:** Except fluorine, all other halogens form four series of oxoacids of the following type.

(a) **HOX (Hypohalous acid):**

HOC*l* (Hypochlorous acid)

HOBr (Hypobromous acid)

HOI (Hypoiodous acid)

The decreasing order of acidity is:

$$H - O - Cl \rightarrow O > H - O - Br > H - O - I$$

(b) **HXO_2 (Halous acid) :**

$HClO_2$ (Chlorous acid)

$HBrO_2$ (Bromous acid)

HIO_2 (Iodous acid)

The decreasing order of acidity is:

$$H-O-Cl \rightarrow H-O-Br \rightarrow O > H-O-I \rightarrow O$$

(c) **HXO_3 (Halic acid):**

$HClO_3$ (Chloric acid)

$HBrO_3$ (Bromic acid)

HIO_3 (Iodic acid)

The decreasing order of acidity with decrease of electronegativity of halogen

is : $\overset{+5}{HClO_3} > \overset{+5}{HBrO_3} > \overset{+5}{HIO_3}$

(d) **HXO_4 (Perhalic acid):**

$HClO_4$ (Perchloric acid)

$HBrO_4$ (Perbromic acid)

HIO_4 (Periodic acid)

The decreasing order of acidity with decrease of electroneeativity of halogen

is: $HClO_4 > HBrO_4 > HIO_4$

$$\overset{+1}{HOX} < \overset{+3}{HXO_2} < \overset{+5}{HXO_3} < \overset{+7}{HXO_4}$$

PREPARATION, PROPERTIES AND USES OF CHLORINE (Cl_2)

Methods of Preparation of Chlorine

(A) From $CaOCl_2$

$$CaOCl_2 + 2HCl \rightarrow Cl_2 + CaCl_2 + H_2O$$

(B) From $KMnO_4$ and cone. HCl:

$$2KMnO_4 + 16HCl\,(aq.) \rightarrow 5Cl_2 + 2KCl + 2MnCl_2 + H_2O$$

(C) Thermal decomposition of chlorides of Noble metals:

$$Pt\,Cl_4 \xrightarrow{\Delta 374^0\,C} Cl_2 + Pt\,Cl_2$$

$$Pt\,Cl_2 \xrightarrow{582^0\,C} Cl_2 + Pt$$

$$Au\,Cl_3 \xrightarrow[\Delta]{175^0\,C} Cl_2 + AuCl$$

$$2Au\,Cl \xrightarrow{185^0\,C} Cl_2 + 2Au$$

(D) **Deacons process :** $4\,HCl + O_2 \xrightarrow{CuCl_2\ 723K} 2Cl_2 + 2H_2O$

(E) **Electrolysis of brine.**

Physical properties :

- (i) It is greenish yellow coloured gas with pungent smell.
- (ii) It is partly soluble in water.
- (iii) The B.P. is 239 K.
- (iv) The B.E. is more than F_2 i.e. -242.6 kJ/mole.

In spite of smaller bond length it has lower b.E. due to electroning (unshared electron) repulsion.

Chemical properties of Chlorine :

$$Cl_2 \longrightarrow \left|\begin{array}{ll}
\xrightarrow{H_2} & HCl \\
\xrightarrow{B} & BCl_3 \\
\xrightarrow{P} & PCl_3 \\
\xrightarrow{metal} & \text{Metal chloride} \\
\xrightarrow{H_2O} & (HCl + HClO)\ \text{or}\ (2HCl + O) \\
\xrightarrow{NaOH(cold)} & NaClO + NaCl + H_2O \\
\xrightarrow{NaOH\ (hot)} & NaClO_3 + NaCl + H_2O \\
\xrightarrow{Ca(OH)_2} & CaOCl_2.H_2O\ \text{(Belaching powder)} \\
\xrightarrow[Cl_2\ excess]{NH_3\ (less)} & NCl_3 + HCl \\
\xrightarrow{H_2S} & HCl + S \\
\xrightarrow{SO_2 + H_2O} & H_2SO_4 \\
\xrightarrow{HBr/HI} & Br_2\ (or)\ I_2
\end{array}\right.$$

$$\left|\begin{array}{ll}\xrightarrow{SO_2} & SO_2Cl_2 \\ \xrightarrow{C_2H_4} & C_2H_4Cl_2 \\ \xrightarrow{SO_3^{2-}} & SO_4^{2-} \\ \xrightarrow{S_2O_3^{2-}} & SO_4^{2-}+S \\ \xrightarrow{FeCl_2} & FeCl_3 \\ \xrightarrow{FeSO_4+H_2SO_4} & Fe_2(SO_4)+HCl \\ \xrightarrow{Aq\ KI} & KCl+I_2 \\ \xrightarrow{CH_4} & CH_3Cl+CH_2Cl_2+CHCl_3+CCl_4\end{array}\right.$$

Uses of Chlorinse

(i) It is used for the bleaching of pulp, textiles etc.

(ii) It is used for the manufacture of chloroform, CCl_4 PVC, phosgene.

PREPARATION OF HYDROGEN CHLORIDE

In laboratory, it is prepared by heating sodium chloride with concentrated sulphuric acid.

$$NaCl+H_2SO_4\xrightarrow{420K}NaHSO_4+HCl$$

$$NaHSO_4+NaCl\xrightarrow{823K}Na_2SO_4+HCl$$

HCl gas can be dried by passing through concentrated sulphuric acid.

Physical Properties of Hydrogen chloride

(i) HCl gas is a colourless and pungent smelling gas.

(ii) It is extremely soluble in water and ionises as follows :

$HCl(g) + H_2O(l) \rightarrow H_3O^+ (aq) + Cl^-(aq)\ K_a = 10^7$

Its aqueous solution is called hydrochloric acid. High value of dissociation constant (K_a) indicates that it is a strong acid in water.

Gaseous state is non-conductor while in solution it conducts electricity due to ionisation.

Chemical Properties of Hydrogen chloride

(i) It reacts with NH, and gives white fumes of NH_4Cl.

$NH_3 + HCl^3 \rightarrow NH_4Cl$

(ii) When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, like gold, platinum.

$Au + 4H^+ + NO_3 + 4Cl^- \rightarrow AuCl_4^- + NO + 2H_2O$

$3Pt + 16H^+ + 4NO_4^- + 18Cl^- \rightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$

(iii) Hydrochloric acid decomposes salts of weaker acids, like carbonates, hydrogen-carbonates, sulphites, etc.

$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2\uparrow$

$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2\uparrow$

$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2\uparrow$

$Na_2S + 2HCl \rightarrow 2NaCl + H_2S\uparrow$

Uses of Hydrochloric acid

(i) In the manufacture of chlorine, NH_4Cl and glucose (from corn starch).

(ii) As a laboratory reagent.

OXOACIDS OF HALOGENS

Fluorine forms only one oxoacid, due to high electronegativity and small size. HOF is known as fluoric (I) acid or hypofluorous acid. The other halogens form several oxoacids. Most of them cannot be isolated in pure state. They are stable only in aqueous solutions or in the form of their salts.

INTER-HALOGEN COMPOUNDS

The compounds containing two or more halogen atoms are called **interhalogen compounds.**

All the interhalogen compounds are covalent and more diamagnetic in nature. They are unstable, volatile and reactive than component halogens. This is because of the fact that the electronegativity difference between the halogen atoms in the compound is negligible.

Types of Interhalogen compounds:

Four types of interhalogen compounds are AX, AX_3, AX_5 and AX_7.

(A = Less electronegative halogen, X = more electronegative halogen)

(i) AX_3 type:

ClF, BrF, BrCl, ICl, IBr and IF (unstable) Structure - Linear

(ii) AX_3 type:

Structure - **T shaped**

ClF_3, BrF_3, ICl_3, IF_3 (unstable) are the examples of AX_3 type compound.

(iii) AX_5 type:

Structure - Square pyramidal

BrF_5, IF_5 are the examples of AX_5 type compound.

(iv) AX_7 type:

Structure - **Pentagonal bipyramidal**

IF_7 (unstable) is the only example of AX_7 type compound.

PSEUDO HALOGENS AND PSEUDO HALIDES

The pseudo halides are uninegatively charged ions composed of two or more electronegative atoms which have properties similar to halide ions.

Example:	CN^-	OCN^-	SCN^-
	(cyanide)	(ocyanate)	(thiocyanate)

These are diatomic molecule having similarities with halogens.

Example:	$(CN)_2$	$(SCN)_2$,	$(OCN)_2$
	Cyanogen	Thiocyanogen	Oxycyanogen

HOME ASSIGNMENT

1. (a) Bromine turns starch Iodine paper ______.

   (b) Chlorine water acts as a ________ reagent.

   (c) NaI (s) with conc. H_2SO_4 possibly liberates _____ gas.

   (d) The formula of bleaching powder is _______.

   (e) The halogen with highest bond dissociation energy is _______ .

2. How does ‘F’ differ from other elements of the group ?

3. Provide the laboratory method of preparations of

   (i) Cl_2 (ii) HCl (iii) HBr

4. What happens when

   (i) $Cl_2(g)$ pass through NH_3 ?

   (ii) $Cl_2(g)$ through aqueous solution of H_2S ?

5. Predict the hybridisation and shape of ______

   ClF_3, ClO_4^-, ClO_3^-, IF_5, ClO_2^-

6. What are interhalogen compounds ? Compare the reactivity of halogen and interhalogen compounds.

Lecture -48-49 :

Group - 18
NOBLE GASES

* Elements He, Ne, Ar, Kr, Xe, R_n^*, element 118 $\left(O_g\right)$

Stable isotope = $^{294}_{118}O_g \left(t_{1/2} = 0.89 \,\text{milli second}\right)$

O_g = oganesson (unun octium=118)

* Relative aboundance : Ar > Ne > He > Kr > Xe

Argon is the most abundant noble gas $\left(9.3\times10^{-1}\ \%\ \text{by volume}\right)$

Natural gas - 2 – 7 %. He

Minerals Like monazite sand, pitch blende, clevite contain nobles (He).

Sun’s atmosphere also contains He.

Radon is obtained from **Ra.**

$$\underset{(\text{Group}-2)}{^{226}_{88}\text{Ra}^*} \longrightarrow \underset{(\text{Group}\ '\text{O}')}{^{222}_{86}\text{Rn}^*} + ^4_2\text{He}$$

* **Periodic position :** Zero is a position between –1 and +1.

So also Noble gases are placed under Group ‘O’ between most electropositive alkalimetals (+1) and most electronegative halogens (–1).

Halogens (Group17) Noble gases (group 18) Alkalimetals (Group17)

* **Electronic configuration** ns^2np^6 (n=2 to 7) except Helium with configuration (He = $1s^2$)

* **Atomicity or valency** These are all mono-atomic, $Cp/Cv = 1.66$.

Due to absence of unpar electron, $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$ These elements have generally no, combining capacity i.e., these are zerovalent.

* **Solubility in water :** These gases are more soluble than Nitrogen in water. The solubility increases with increase of molecular size, this is due to increased dipole - induced dipole attraction. Solubility in water (dipole) increases from He to Rn with increase of polarisability. Ne and Ar are more soluble in water than Nitrogen.

* **Liquefcation** of noble gas. It increaes from He to Xe as the vander Waals force increases from top to bottom with increase of molecular size. The b.p / m.p. also increases in the same order. He < Ne < Ar < Kr < Xe

ΔiH values : This value decreases from top to bottom with increase of atomic size. This follow the increase of chemical reactivity from He to Xe. KLr and Xe generally form compounds with most electronegative atom from compounds with most electronegative atom such as fluori (4.1) and Oxygen (3.5).

Electro affinity. Due to stable electronic configuration these elements have zero electron affinity. However these have positive $\Delta_{eg}H$ value.

$$Ne_{(g)} + \bar{e}_{(gas)} \longrightarrow N\bar{e} + 116\,kJ/mol$$

$$Xe_{(g)} + \bar{e}_{(gas)} \longrightarrow X_e^- + 77\ kJ/mol$$

Aromic radii :

These have only vander Waals radii (not covalent radii) i.e., the value of is maximum along a period: However this value increases from top to bottom in a group with increase of shell no.

Adsorption by activated charcoal. The extent of adsorption increases with increase of vander Waals force. 'He' has least tendency to be adsorbed or activated chareol.

These elements are fairly good conductors of heat & electricity. Thermal conductivity of He is very gigh at room temperature (even much higher than Cu.)

Chemical reactivity

PtF_6 is a powerful oxidising egent. It oxidies O_2 to O_2^+. ΔiH value of (O_2) is comparable with Xe. So Bartlette thought of Xe compound. The first noble gas compound synthesized is Xe[PtF_6] compared to O_2[PtF_6]

Formation of clathrates Ar, Kr and Xe form clatrates due to of appropriate size these can fit into the cage of host molecules. Host- guest molecule.

$$Xe + F_2 \xrightarrow[673\,K]{Nickel\ tube} \boxed{XeF_2\,(s)}$$

$$Xe + F_2 \xrightarrow{Mercury\ vap.} \boxed{XeF_2\,(s)}$$

$$Xe + O_2F_2 \xrightarrow{155K} \boxed{XeF_2\,(s)}$$

$$\boxed{XeF_2\,(s)} \xrightarrow{+H_2} Xe + HF$$

$$\boxed{XeF_2\,(s)} \xrightarrow{+H_2O} Xe + HF + O_2$$

$$\boxed{XeF_2\,(s)} \xrightarrow{HCl} Xe + HF + Cl_2$$

$$\boxed{XeF_2\,(s)} \xrightarrow{PF_5} [XeF][PF_5]$$

Fluorido Xe (II) penta fluoridophospate(iv)

$$\boxed{XeF_2\,(s)} \xrightarrow{SbF_5} [XeF_3][SbF_6]$$

Uses : (i) Fluorinating agent (ii) To prepare Xe on reduction

$$XeF_2 + H_2 \longrightarrow Xe + 2\,HF$$

Structure : Linear, sp^3d hybrididation, $AB_2\,L_3$.

→ $\boxed{XeF_4}$

$$Xe_{(g)} + 2F_{2(g)} \xrightarrow[193\,K]{electronic\ discharge} \boxed{XeF_4\,(s)}$$

$2-15\,mm.\,pressure$

$$Xe_{(g)} + F_{2(g)} \xrightarrow[400^0C,\ atm\ pressure]{Ni\ vessel} \boxed{XeF_4\,(s)}$$

$1:5$

$$\boxed{XeF_4\,(s)} \xrightarrow{+H_2} Xe + HF$$

$$\boxed{XeF_4\,(s)} \xrightarrow{H_2O} Xe + XeO_3 + HF + F_2$$

$$\boxed{XeF_4\,(s)} \xrightarrow{KI} Xe + HF + I_2$$

$$\boxed{XeF_4\,(s)} \xrightarrow{HCl} HF + Xe + Cl_2$$

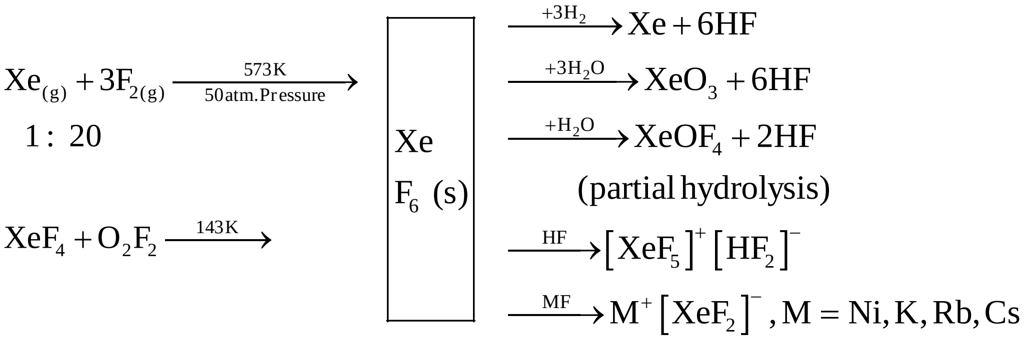
$$\boxed{XeF_4\,(s)} \xrightarrow{SbF_5} [XeF_3][SbF_6]$$

$$\boxed{XeF_4\,(s)} \xrightarrow{Pt} Xe + Pt\,F_4$$

$$\boxed{XeF_4\,(s)} \xrightarrow{SF_4} Xe + SF_6$$

Structure : $Sp^3\,d^2$ hybridisation, AB_4L_2, shape square planar

→ $\boxed{XeF_6}$



Structure : (XeF_6) Hybridisation sp^3d^3, AB_6L,
Shape- distorted octahedral.

* **Uses of noble gases :**

Helium :

(i) Filling airstrips and balloons, inflating tyres of big aeroplanes.

(ii) Releif in respiratory disease for artificial breathing.

(iii) Respiration of sea divers. He and oxygen (20 **:** 80) in place of nitrogen which gets disolved in blood under water pressusre. On coming out the sea, diver feels painfull sensation when blood releases the dissolved N_2(g). This is called bends. Helium remains undissolved.

(iv) Gas thermometer

(v) Welding of reactive metal in an inert atmosphere of He.

(vi) Production of low temperature (4.2 K)

(vii) Clinical diagonsis (In MRI)

Neon :

(i) production of coloured glow

(ii) Beacon light for signalling through fog & mist.

(iii) In electrical device like voltage stabiliser, current rectifier.

Argon :

(i) Electrical bulbs and radio valves.

(ii) To produce inert atmosphere.

(iii) Coloured glow : (Ar + Hg vapour) blue / green colour in the discharge tube.

Kr & Xe : Filling electric bulbs & tubes (better than Ar)

Radon : (i) Treatment of cancer (radio therapy)
(ii) Detection of defect in steed casting.

HOME ASSIGNMENT

a. **Fill in the blanks :-**

(i) _____ gas is used for artificial respiration in place of N_2.

(ii) The first noble gas compound synthesised was ________ .

(iii) ______ is the most abundant noble gas.

(iv) Shape of XeF_4 is ________.

(v) The noble gas with exceptional electronic configuration is _____.

b. Account for the following :

(i) Hydrogen is di-atomic while 'He' is monoatomic.

(ii) XeO_3 and SO_3 are not of identical shape.

(iii) Noble gases are included as zero group elements.

(iv) The solubility of noble gases in water increases from He to Xe.

(v) Xe forms compounds with 0 and F.

C. Write down the uses of XeF_4, Xe, Ne, Ar.

D. Predict the hybridisation and shape of : $XeOF_2$, $XeOF_4$, $XeO_2 F_2$, $[XeO_4]^{2-}$.

L-50, 51, 52

UNIT - VIII
d- BLOCK ELEMENTS
TRANSITION METALS

A transition metal may be defined as one that has an incomplete inner d-orbital, i.e., d-block of elements.

The general electronic configuration of transition elements is (n-1) $d^{1\text{-}10}$ n $s^{1 \text{ or } 2}$

In the case of d-block (transition) elements, electrons are added successively to the (n-1) d-orbitals. $_{24}Cr\ 3d^5\ 4s^1$ and $_{29}Cu\ 3d^{10}\ 4s^1$ configuration is due to exceptional stability of half filled (d^5) and full filled d^{10} orbitals.

The elements are called transition elements as they are placed between the s- and p-block elements and their properties represent a transition between the highly reactive electropositive elements of the s-block and the electronegative elements of the p-block.

As shown above the d-block elements belong to groups 3 to 7, 8 and 11 to 12 of the periodic table.

These transition elements are present in the periodic table in four series.

4th period - Sc_{21} – Zn_{30}

5th period Y_{39} Cd_{48}

6th period La_{57}* Hg_{80}

7th period AC_{89}* Cn $_{112}$ (coper nicium)

* Lanthanides and actinides placed separately at the bottom of periodic table.

Lanthanides and Actinides

Inner transition elements contain incomplete 4fand 5forbitals respectively in addition to their incomplete (n-l)d orbitals. Inner transition elements are special type of transition elements. The elements Zn, Cd and Hg remain at the end of3d,4d and 5d series respectively whose atoms have completely filled d-orbitals for which they are non-transitional.

The first transition series : The first transition series or 3d-series is present in the 4th period of the periodic

GENERAL CHARACTERISTICS OF TRANSITION ELEMENTS :

Transition elements are solid metals hard,malleable and ductile. Thy have relatively high densities, high melting points and high boiling points. These properties indicate that the atoms in these elements are held together by strong metallic bonds. Such metallic bonds are even present in their molten states. The properties of transition (d-block) elements are intermediate between the properties of s and p block elements.

1. Atomic radii:

The atomic radii of the transition elements of a particular series decrease slightly with increase in atomic number. In the case of these elements, the electrons are added successively to the inner (n-l)d orbitals and these electrons screen the outer ns electrons from the nucleus. The effective nuclear charge Z^* thus increases slightly. Therefore, there is a slight decrease in atomic radii.

In the first transition series the atomic radius value increases from Ni $(1.24\overset{0}{A})$ to Cu $(1.28\overset{0}{A})$. This is due to increased force of repulsion between added electrons which overcome effective nuclear charge (nuclear attraction force).

2. lonisation enthalpy $(\Delta_i H)$:

lonisation enthalpies of transition elements increase across a transition series with increase in atomic number. This trend is, however, not regular. This is because though the nuclear charge increases, the screening effect of added electrons also increases. These two effects almost cancel each other. lonisation enthalpies are in between s- and p- block elements and these elements are less electropositive than s-block elements. Zinc, cadmium and mercury have comparativly higher ionisation enthalpy values, because they have stable outer electronic configuration, $(n\text{-}l)d^{10}\ ns^2$.

There is a general increase in the second ionisation enthalpy as the atomic number increases. The exception is manganese. The second ionisation enthalpy of Cr and Cu involves the removal of one electron from the 4s orbital and another electron from the half-filled and completely filled 3 d-orbital respectively. The half-filled and filled orbitals have extra stability associated with them. Therefore, the second ionisation enthalpy of these elements are relatively larger. Eventhough transition elements form ionic compounds, the tendency is less than the s-block elements. In higher valency state, there is also a tendency for covalent bond formation.

3. Metallic properties :

Transition elements are all hard metals except mercury which is a liquid.These elements are harder and more brittle than s-block elements.

The atoms in these elements are held together by strong metallic bonds. The strength of such metallic bonding depends upon the interaction between the electrons in the outermots shell. In general, the greater the number of valence electrons available, the stronger is the bond. Further electrons in the (d-orbitals form stronger metallic bonds. In transition elements a minimum of three electrons, $(n\text{-}1)d^x\ ns^2$ are available for interaction with other atoms for the metallic bond formation.Again greater the number of unpaired electrons greater is the strength of the bond. In the first transition series Cr is very hard having five unpaired d- electrons. In the case of $_{30}Zn$, $(3d^{10}\ 4s^2)$, the metal is not hard because there is complete pairing of 3d electrons. In the third transition series $Hg_{80}(5d^{10}\ 6s^2)$ having complete pairing of 5d electrons exists as a liquid. These metals are, as expected, good conductors of heat and electricity.

4. **Denisities, melting and boiling points :**

The high densities of transition elements are due to their relatively small atomic radii. The densities of the first transition series elements increase across the period with the increase in atomic number.

Transition elements have high melting and boiling points. The high melting and boiling points are due to strong inter-atomic bonding which invloves the participation of both 4s and 3d electrons.

5. **Variable oxidation states :**

Transition elements show more than one oxidation states in their compounds. The oxidation states shown by the first transition series are given in $Cr^{(+2 \text{ to } +6)}$ and $Mn^{(+2 \text{ to } +7)}$ have a wide variation of o.s. in their compounds.

Transition metals have their valence electrons in two different sets of orbitals ns and (n-l)d which have nearly the same energies. All these elements use their two ns electrons and thus show +2 oxidation states. When oxidation states are greater than +2, the unpaired (n-1)d electrons are involved in bonding in addition to the **ns** electrons. The elements thus show +3 and higher oxidation states besides +2 oxidation state. Scandium has exclusively an oxidation state of +3. In the case of tansition elements the oxidation states vary by one unit whereas in some of the p-block elements variable oxidation states marked by a difference of two units. This is due to the inert pair effect. Thallium shows oxidation states +1 and +3 and lead has two oxidation states +2 and +4.

6. **Formation of coloured compounds :**

Majority of transition metal compounds are coloured. In contrast the compounds of s-and p-block elements are often colourless or are generally not strongly coloured. When a compound absorbs light of a particular wavelength,it is able to promote an electron from one energy level to another higher energy level.

If E, is the energy associated with the electron in one energy level and E_2, the energy associated with the electron in the higher energy level, then $E_2 - E_1 = \Delta E$ i.e. energy of absorbed light or radiation. Since $\Delta E = h\nu = h\frac{c}{\lambda}$, the energy of absorbed radiation is inversely proportional to the wavelength λ Coloured substances such as compounds of transition elements absorb in the visible region 4000-7500 $\overset{0}{A}$ or longer wavlength. Colourless substancees such as compounds of s-and p- block elements absorb in the u.v(ultraviolet) region below 4000 $\overset{0}{A}$ or shorter wavelength.

The compounds of transition metals are coloured due to the presence of unpaired d-electrons in the partly filled d- orbitals of the metal. Here the light radiation is absorbed in the visible region (λ =4000 -7500 A) with a fairly small energy to promote d-electron to a higher energy level within the d- orbital, resulting **d- d transitions of electrons**. The colour of the compound is complementary to the oabsorbed colour. $CuSO_4.5H_2O$ is blue in colour since it absorbs orange colour from visible light (λ - 6000 - 6500A^0) and emits the complementary colour blue (blue is complementary to orange).

The compounds of Sc^{3+} ($3d^0\ 4s^0$) and Zn^{2+} ($3d^{10}\ 4s^{\circ}$) are colourless because they do not contain any unpaired d-electron.

Colour shown by some hydrated transition metal ions.

Ion	Outer electronic Configuration	No. of unpaired electrons	Colour
Sc^{3+}	$3d^0$	0	Colourless
Ti^{3+}	$3d^1$	1	Purple
V^{3+}	$3d^2$	2	Green
Cr^{3+}	$3d^3$	3	Violet
M_n^{+}	$3d^4$	4	Violet
Mn_2^{+}	$3d^5$	5	Pink
Fe^{3+}	$3d^5$	5	Yellow
Fe^{2+}	$3d^6$	4	Green
Co^{2+}	$3d^7$	3	Pink
Ni^{2+}	$3d^8$	2	Green
Cu^{2+}	$3d^9$	1	Blue
Cu^{2+}	$3d^{10}$	0	Colourless
Zn^{2+}	$3d^{10}$	0	Colourless

7. Formation of Complex compounds:

Transition metal ions have greater tendency to form complexes in contrast to s- and p– block elements.This is because the transition metals have (i) small size of highly charged cations and (ii) vacant inner d-orbitals of approximately the same energy to accept lone pairs of electrons donated by the ligands and (iii) high effective nuclear charge in the cation.

In a complex, a central atom or ion is surrounded by a number of ligards as per their secondary valency. The bonding between ligand and the transition metal ion can be either predominantly electrostatic or predominantly covalant.In many cases the attachment of ligands to the central metal atom or ion is by coordinate covalent bonds. The number of attached ligands is called coordination number (C.N) of the central metal atom or ion. The complex is said to be unstable if the ligands are easily removed. If it is difficult to remove the ligands from the complex, then the complex is stable one.

Complex ions such as $[Cu(NH_3)_4]^{2+}$ (tetramminecopper (II) ion),
$[\ Fe(CN)_6]^{4-}$ (hexacyanid oferrate(II) ion) and $[Fe(CN)_6]^{3-}$ (hexacyanidoferrate (III)) are well known.

In Tetrammine copper (II) sulphate, Tetrammine copper (II) cation, since ammonia is a neutral ligand, the charge 2+ on Cu is transferred on to the total complex ion indicated by square bracket. In this complex, the complex ion is a cation and thus the complex is called a cationic complex. In this complex, the coordination number of Cu is 4.

While the complex potassium ferrocyanide, is an anionic complex, $[Fe(CN)_6]^{4-}$

9. Paramagnetism:

Transition metals and their compounds are paramagnetic in nature i.e. they are attracted by magnetic field. Paramagnetism arises due to the presence of unpaired d-electrons. These electrons can be regarded as spinning around their axes, just as an electric current through a wire generates a magnetic moment. Magnetic moment due to electron spin is given by $\mu_{eff} = \sqrt{n(n+2)}BM$ where n = number of unpaired electrons.A substance becomes strongly paramagnetic if it contains more number of unpaired electrons. Mn^{2+} ($3d^5$ $4s^0$) and Fe^{3+} ($3d^5 4s^0$) are most paramagnetic, whereas Sc^{3+} ($3d^0$ $4s^0$)and Zn^{2+} ($3d^{10}$ $4s^0$) are diamagnetic in nature. A diamagnetic (non-magnetic) substance is repelled by a magnetic field. In such cases, the paired electrons possess opposite spins and cancel the magnetic moments. In the case of Fe, Co and Ni the spins of the unpaired electrons are much pronounced-as a result, these elements are much more paramagnetic than the rest of the elements. These element are called ferromagnetic which means that they can be magnetised.

10. Catalytic activity ;

Many transition metals and their compounds show catalytic activity due to their variable oxidation states. In the variable oxidation states these are capable of forming unstable intermediate compounds with catalysts. The metal ions while functioning as catalysts change their oxidation states. They can also provide greater surface area for the reactants to the adsorbed and thus come closer to one another for the reaction to occur readily on their (catalyst)surfaces.

The catalytic activity of nickel in the hydrogenation of oils, the use of platinum and vanadium pentoxide, V_2O_5 in the contact process for manufacturing sulphuric acid and the use of iron in Haber's process for manufacturing ammonia are well known.

11. Alloys and interstitial compounds :

Transition metals form intermetallic alloys because they have atoms of nearly the same size. Their atoms can mutually substitute each other in the metal lattice. They also form interstitial alloys like stainless steel, chrome steel etc. Transition metals form interstitial compounds. In interstitial hydrides, the hydrogen is accommodated in the lattice of the transition element. Interstitial nitrides and carbides of transition metals are known, which are similar to interstitial hydrides in structure.

POTASSIUM DICHROMATE, $K_2Cr_2O_7$

It is an important oxidant used for preparation of many compounds. Besides it finds its use in leather industry.

Flow chart of preparation :

$$\boxed{\text{chromite ore, } FeCr_2O_4} \xrightarrow[\text{Fused}]{Na_2CO_3+O_2} \boxed{\begin{array}{c}\text{Sodium chromate}\\ \text{(Yellow)}\end{array}} \xrightarrow{H_2SO_4} \boxed{\begin{array}{c}Na_2Cr_2O_7.2H_2O\\ \text{Orange}\end{array}}$$

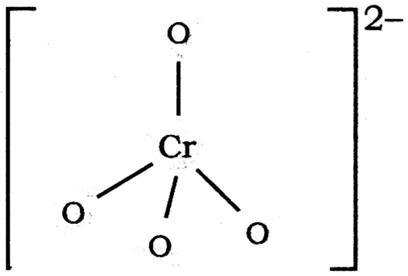
$$\xrightarrow[\text{hot}]{\text{Solution KCl}} \boxed{\begin{array}{c}K_2Cr_2O_7 \text{ orange red}\\ \text{(crystal)}\end{array}}$$

CrO_4^{2-} & $Cr_2O_7^{2-}$ ions are interconvertible in aqueous solution depending on pH.

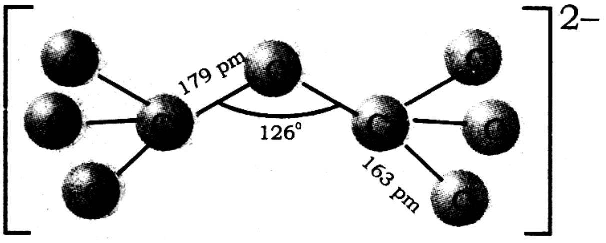
$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$

Structure of CrO_4^{2-} & $Cr_2O_7^{2-}$



Chromate ion



Dichromate ion

Physical properties :

Potasium dichromate form orange red crystals melting at 671K. It is moderately soluble in cold water but highly soluble in hot water.

Chemical properties :

$K_2Cr_2O_7$

$[Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr_r^{3+} + 7H_2O$

$\xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$

$\xrightarrow{14HCl} 2kCl + 2CrCl_3 + 7H_2O + 3Cl_2$

$\xrightarrow[\text{conc.}H_2SO_4]{4NaCl+} 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 \uparrow + 2H_2O$

red vapour

$\downarrow (CH_3COO)_2 Pb$

$PbCrO_4 \downarrow$

(yellow)

$\xrightarrow{I^{(-)}} I_2$

$\xrightarrow{Fe^{2+}} Fe^{3+}$

$\xrightarrow{H_2S} S$

$\xrightarrow{2H_2O+SO_2} SO_4^{2-} + 4H^+ + 2e^-$ (green colouration due to $Cr_2(SO_4)_3$

$\xrightarrow{SO_3^{2-}+H_2O} SO_4^{2-} + 2H^+ + 2e^-$

$\xrightarrow{2KOH} 2K_2CrO_4 + H_2O \xrightarrow{H_2SO_4} K_2Cr_2O_7 + K_2SO_4 + H_2O$

Yellow

$\xrightarrow{CH_3-CH_2OH} CH_3CHO \xrightarrow{(O)} CH_3COOH,$

$CH_3CH_2OH \longrightarrow CH_3CHO + 2H^+ + 2e^-$

Uses :

(i) In volumetric analysis for estimation of Fe^{2+}, I^- ions.

(ii) In the preparation of several chromium compounds like $ZnCrO_4$, $PbCrO_4$ etc.

(iii) In photography for hardening film (gelatin)

(iv) As a cleansing agent ($K_2Cr_2O_7$ + Conc H_2SO_4) for glassware.

(v) In dyeing, chrome tanning etc.

Potassium Permanganate :

Physical properties:

Potasium permanganate forms dark purple (almost black) crystal.

It is not very much soluble in water, about 6.4 gms dissolving in 100 gms of water at 293K.

Both manganate and permanganate ions are tetrahedral. The green manganate is paramagnetic with one unpaired electron whereas the purple permanganate is diamagnetic.

The π bonding is due to overlap of p-orbital of oxygen with d-orbital of manganese.

Tetrahedral manganate ion (green)   Tetrahedral permanganate ion (purple)

Flow chart of preparation :

$$\boxed{\text{Pyrousite ore, MnO}_2} \xrightarrow[\Delta]{\mathrm{KOH+O_2}} \boxed{\mathrm{K_2M_nO_4}} \xrightarrow[\text{Anodic oxidation}]{\mathrm{Cl_2/ozone/CO_2}} \boxed{\mathrm{KMnO_4}}$$

(green mass)   dark purple

e.g. $2\ \mathrm{K_2M_nO_4} + \mathrm{Cl_2} \rightarrow 2\ \mathrm{KCl} + 2\ \mathrm{KMnO_4}$

Chemical properties : $2\mathrm{KMnO_4} \xrightarrow{\Delta} \mathrm{K_2MnO_4} + \mathrm{MnO_2} + \mathrm{O_2}$

$$2\mathrm{KMnO_4} + 4\mathrm{KOH} \longrightarrow 4\mathrm{K_2MnO_4} + 2\mathrm{H_2O_2} + \mathrm{O_2}$$

Oxidising character **(i)** Acidic $\mathrm{MnO_4} + 8\mathrm{H^+} + 5e^- \rightarrow \mathrm{Mn^{2+}} + 4\mathrm{H_2O}$

(ii) Alkaline $\mathrm{MnO_4^-} + e^- \longrightarrow \mathrm{MnO_4^{2-}}$

(iii) Neutral $\mathrm{MnO_4^-} + 2\mathrm{H_2O} + 3e^- \longrightarrow \mathrm{MnO_2} + 4\mathrm{OH^-}$

$\mathrm{KMnO_4}$

$\xrightarrow{\mathrm{FeSO_4}}$ $\mathrm{Fe_2(SO_4)}$, $\mathrm{Fe^{2+}} \longrightarrow \mathrm{Fe^{3+}} + e^-$

$\xrightarrow{\mathrm{KI}} \mathrm{I_2}$ $2\mathrm{I^-} \longrightarrow \mathrm{I_2} + 2e^-$

$\xrightarrow{\mathrm{H_2S}}$ S $\mathrm{H_2S} \longrightarrow \mathrm{S} + 2\mathrm{H^+} + 2e^-$

$\xrightarrow{\mathrm{KNO_2}}$ $\mathrm{KNO_3}$ $\mathrm{NO_2^-} + \mathrm{H_2O} \longrightarrow \mathrm{NO_4^{2-}} + 4\mathrm{H^+} + 2e^-$

$\xrightarrow{\mathrm{H_2C_2O_4}}$ $2\mathrm{CO_2} + \mathrm{H_2O}$ $\mathrm{C_2O_4^{2-}} \longrightarrow 2\mathrm{CO_2} + 2\mathrm{I^-}$

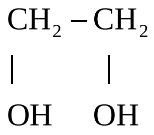
$\xrightarrow{\mathrm{HX}} \mathrm{X_2}$ $2\mathrm{X^-} \longrightarrow \mathrm{X_2} + 2e^-$

$\xrightarrow{\mathrm{MnSO_4}}$ $\mathrm{MnO_2} + \mathrm{H_2SO_4}$ $\mathrm{M_n^{2+}} + 2\mathrm{H_2O} \longrightarrow \mathrm{MnO_2} + 4\mathrm{H^+} + 2e^-$

$\xrightarrow{\mathrm{Na_2S_2O_3}}$ $\mathrm{Na_2SO_4} + \mathrm{S}$, $2\mathrm{MnO_4^-} + \mathrm{O_3^=} + \mathrm{H_2O} \longrightarrow 2\mathrm{MnO_2} + 3\mathrm{SO_4^{2-}}$
$+ 3\mathrm{S} + 2\mathrm{OH^-}$

$\xrightarrow{\mathrm{I_2}} \mathrm{IO_3^-}$ $\mathrm{I_2} + 6\mathrm{H_2O} \longrightarrow 2\mathrm{IO_3^-} + 12\mathrm{H^+} + 10e^-$

$\xrightarrow{\mathrm{CH_2{=}CH_2(OH^-)}}$



$\mathrm{CH_2(OH)-CH_2(OH)}$

Uses:

(1) In qualitative analysis for detection ofhalides, sulphites, oxalates etc.
(2) In volumetric estimations.
(3) In the manufacture of saccharine, benzoic acid, acetaldehyde etc.
(4) As a disinfectant.
(5) Alkaline $KMnO_4^-$ soln. is Baeyer's reagent which finds its use in organic reactions.

HOME ASSIGNMENT

(a) What are transitional elementts ?
(b) Explain the following
  (i) $KMnO_4$ is economical in acidic medium in quantitative analysis.
  (ii) SO_2 (g) decolorises purple colour of $KMnO_4$ solution.
  (iii) Transition metals form alloys.
  (iv) $CuSO_4$ is paramagntic while $ZnSO_4$ is diamagnetic.
  (v) Transition metals exhibit variable valency.
(c) Balance the following :

$$MnO_4^- + H_2S \longrightarrow MnO_2 + S + H_2O + OH^-$$

$$MnO_4^- + H^+ + NO_2^- \longrightarrow M_n^{2+} + NO_3^- + H_2O$$

$$Cr_2O_7^{2-} + H^+ + SO_3^{2-} \longrightarrow Cr^{3+} + SO_4^{2-} + H_2O$$

(d) Mention the chromylchloride test for Cl^-.

Lecture -53

f-block elements

Introduction :

The elements in which the last electron enters the ante-penultimate energy level, i.e. (n-2) f-orbitals are called f-block elements. They are also regarded as inner transition metals / rare earth metals (due to their occurence in traces in nature).

The f-block elements consists of two series :

Lanthanoids : The group of 14 elements following Lanthanum (Z = 5 8 to 71) are known as Lanthanoids.. Lanthanum though a d-block element, is included in any discussion of lanthanoids because it closely resembles them in its properties. The study of lanthanoids is comparatively easier because they show only one stable oxidation state.

Actinoids : The group of 14 elements following Actinium (Z = 90 to 103) in which the last electron enters into the '5f orbital are known as "Actinoids". Actinium also resembles them in its properties. The elements of this series are radioactive and exhibit complicated gradation in properties. They show wide range of oxidation states.

THE LANTHANOIDS :

(i) Electronic Configuration :

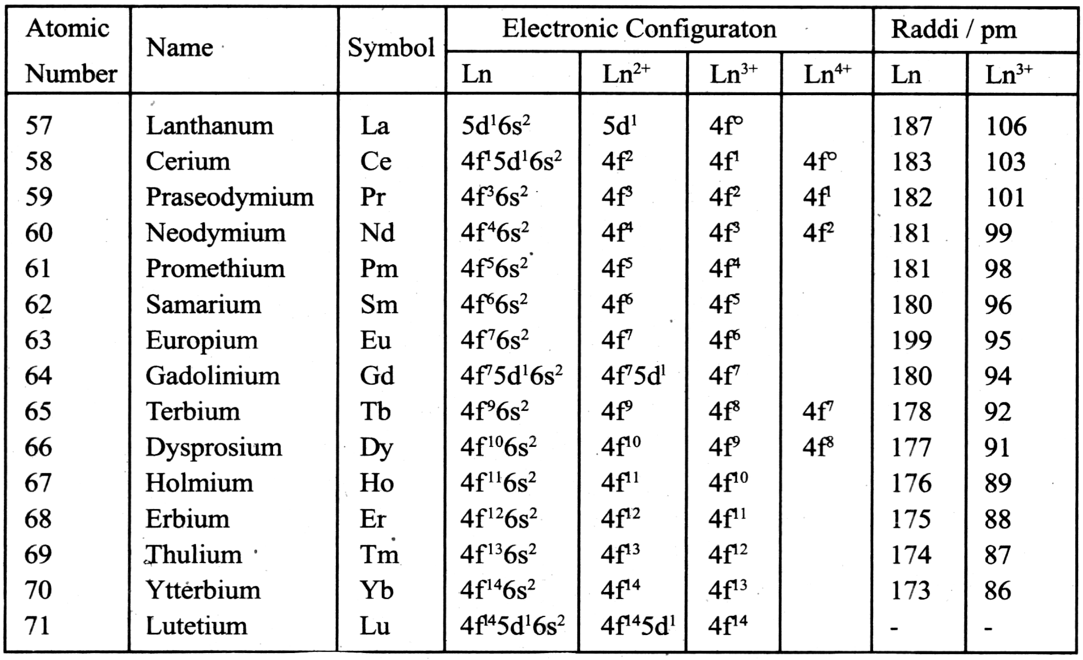
Lanthanoids possess common electronic configuration $6s^2\ 5d^{0-1}\ 4f^{1-14}$. The exceptional electronic configuration of few elements can be explained on the basis of stability.

(i) The electronic configuration of Cerium (Z= 58) is $4f^2\ 5d^0 6s^2$.

(ii) Europium (Z = 63) has electronic configuration $4f^7\ 6s^2$ and that of Gadolinium is $4f^7\ 5d^1\ 6s^2$, because of the extrastability due to half-filled orbitals.

(iii) Ytterbium (Z = 70) has electronic configuration $4f^{14}\ 6s^2$ and Lutetium (Z=71) is $4f^{14}5d^16s^2$, which is explained on the basis of extra stability of the completely filled 4f orbitals.

Table-1 Electronic Configuration and Radii of Lanthanum and Lanthanoids



Atomic Number	Name	Symbol	Electronic Configuraton				Raddi / pm	
			Ln	Ln^{2+}	Ln^{3+}	Ln^{4+}	Ln	Ln^{3+}
57	Lanthanum	La	$5d^16s^2$	$5d^1$	$4f^0$		187	106
58	Cerium	Ce	$4f^15d^16s^2$	$4f^2$	$4f^1$	$4f^0$	183	103
59	Praseodymium	Pr	$4f^36s^2$	$4f^3$	$4f^2$	$4f^1$	182	101
60	Neodymium	Nd	$4f^46s^2$	$4f^4$	$4f^3$	$4f^2$	181	99
61	Promethium	Pm	$4f^56s^2$	$4f^5$	$4f^4$		181	98
62	Samarium	Sm	$4f^66s^2$	$4f^6$	$4f^5$		180	96
63	Europium	Eu	$4f^76s^2$	$4f^7$	$4f^6$		199	95
64	Gadolinium	Gd	$4f^75d^16s^2$	$4f^75d^1$	$4f^7$		180	94
65	Terbium	Tb	$4f^96s^2$	$4f^9$	$4f^8$	$4f^7$	178	92
66	Dysprosium	Dy	$4f^{10}6s^2$	$4f^{10}$	$4f^9$	$4f^8$	177	91
67	Holmium	Ho	$4f^{11}6s^2$	$4f^{11}$	$4f^{10}$		176	89
68	Erbium	Er	$4f^{12}6s^2$	$4f^{12}$	$4f^{11}$		175	88
69	Thulium	Tm	$4f^{13}6s^2$	$4f^{13}$	$4f^{12}$		174	87
70	Ytterbium	Yb	$4f^{14}6s^2$	$4f^{14}$	$4f^{13}$		173	86
71	Lutetium	Lu	$4f^{14}5d^16s^2$	$4f^{14}5d^1$	$4f^{14}$		-	-

ii. Atomic and Ionic sizes :

In the lanthanoid series there is a regular decrease in atomic and ionic radii from Lanthanum to Lutetium. (Table.1). The cumulative effect of this regular decrease (contraction) in the atomic and ionic radii of lanthanoids with increasing atomic number is known as 'Lanthanoid contraction'. Lanthanoid contraction is a unique feature in the chemistry of Lanthanoids.

Cause of Lanthanoid contraction :

Lanthanoid contraction is attributed to the imperfect shielding of one electron by another in the same sub-shell (i.e. 4f), as the '4f orbital is more diffused in space. This imperfect shielding is unable to counter balance the effect of the increased nuclear charge. So the net result is a contraction in size. $\mathrm{ENC}\left(Z^{*} = z - \sigma\right)$ increases.

Consequences ofLanthanoid contraction:

(1) Similarity in size of elements of same group of second and third transition series :

The size of an atom of third transition series is nearly same as that of the atom of the element lying in the same group of the second transition series, due to lanthanoid contraction.

Ex: $_{40}$Zr- 160pm $_{41}$Nb— 146pm
and $_{72}$Hf- 159 pm and $_{73}$Ta - 146 pm

(2) Difficulty in separation Lanthanoids :

The change in sizes of the lanthanoid ions along the series is very small. So their chemical properties are similar with each other and it is difficult to separate the lanthanoids in the pure state. However, the slight difference in sizes results in differences in properties like solubility, hydration, complex ion formation which enable the separation of lanthanoid elements individually by **ion exchange methods.**

(3) Basic character of hydroxides decreases.

(iii) **Oxidation States :**

Lanthanoids possess common oxidation state+3.

The Lanthanoids which acquire a stable configuration of f^0, f^7 or f^{14} by losing 2 or 4 electrons, they show +2 or +4 oxidation state.

Ex. $\mathrm{Eu}^{2-}[\mathrm{Xe}]4f^{7}$; $\mathrm{Yb}^{2+}[\mathrm{Xe}]4f^{14}$

$\mathrm{Ce}^{4+}[\mathrm{Xe}]4f^{0}$; $\mathrm{Tb}^{4-}[\mathrm{Xe}]4f^{7}$

Exceptions :

$\mathrm{Pr}^{4+}[\mathrm{Xe}]4f^{1}$; $\mathrm{Nd}^{2+}[\mathrm{Xe}]4f^{4}$; $\mathrm{Sm}^{2+}[\mathrm{Xe}]4f^{6}$;

$\mathrm{Dy}^{4+}[\mathrm{Xe}]4f^{8}$; $\mathrm{Nd}^{4+}[\mathrm{Xe}]4f^{2}$;

The lanthanoids in +2 or +4 oxidation state tend to show +3 oxidation state by loss or gain of electron.

Sm^{2+} Eu^{4+} and Yb^{2+} ions loose electrons in solutions to show +3 oxidation state and are good reducing agents.

Ce^{4+}, Tb^{+} in their aqueous solution are good oxidising agents as they gain electron and change to +3 oxidation state.

Though the formation of Ce^{4+} is favoured by its noble gas configuration, it has a tendency to show +3 oxidation state and enables it to behave as a strong oxidant.

The E^0 value for Ce^{4-} / Ce^{3+} is + 1.74 V. So it can oxidise water at a very slow rate and Ce (IV) is a good analytical reagent. Praseodymium, Neodymium, Terbium and Dysprosium exhibit +4 oxidation state only in oxides. Their oxides have general formula MO_2 (M = Pr, Nd, Tb or Dy)

(iv) General characteristics of Lanthanoids :

1. **Softness :** All the lanthanoids are silvery white soft metals. They tarnish rapidly in air. Their hardness increases with increasing atomic number. Samarium is exceptionally hard like steel.
2. **Melting points:** The melting points of lanthanoids range between 1000 K to 1200K. Samarium has melting point 1623K..
3. **Thermal and Electrical conductivity :** The lanthanoids have metallic structure. They are good conductors of heat and electricity.
4. **Density:** They have high densities in the range of 6.77 to 9.77 $g.cnT^3$. Their density and other properties vary smoothly with increasing atomic number. Europium and Ytterbium show exceptions.
5. **Colour :** Lanthanoids are silvery white metals. Most of the trivalent metal ions are coloured both in the solid state and in aqueous solution. This is due to f-f transitions of the electrons present in partly filled f-orbitals. The lanthanoid ions with 'n' electrons or (14-n) electrons in f-subshells have similar colour.

   Ex: (a) La^{3+} and Lu^{3+} are colourless, n = 0

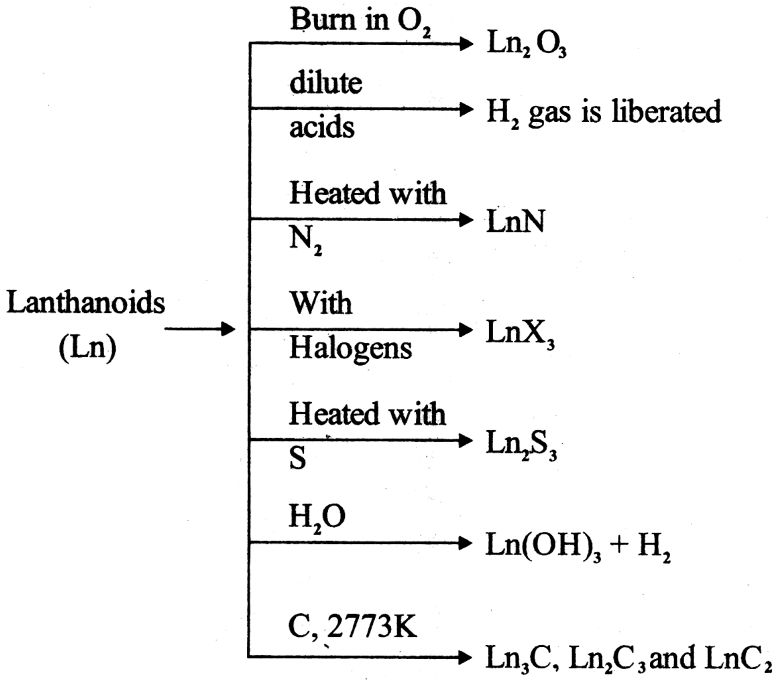
   (b) Sm^{3+} and Dy^{3+} are yellow, n-5

   (c) Eu^{3+} and Tb^{3+} are pink, n = 6
6. **Magnetic behaviour :** The lanthanoid ions are paramagnetic due to presence of unpaired electrons in the 4fsubshell, except La^{3+}, Ce^{4+} (f^0 configuration) and Lu (f^{14} configuration).
7. **Ionisation Enthalpy :** The first IE of lanthanoids are 600 kJ mol^{-1} and second IE are 1200 kJ mol^{-1}. The second lonisation Enthalpy ofLanthnoids are comparable with that of Ca^{2+} That is why the first few members of the series have reactivity similar to Calcium.

   Lanthanum, Gadolinium and Lutetium possess abnormally low values of 3rd lonisation Enthalpy because removal of third electron leads to empty, half-filled and completely filled f-orbitals respectively.
8. **Chemical behaviour:** As discussed previously, the earlier members of lanthanoid series have reactivity similar to Calcium with increasing atomic number they resemble Aluminium in their chemical behaviour.

   (a) **With non-metals :** They combine with hydrogen on gentle heating and form carbides on heating with carbon. With halogens respective halides are formed. Oxides and hydroxides of the type M_2O_2 and $M(OH)_3$ are formed due to reaction with oxygen and water respectively, which are basic in nature.

(b) With dilute acids : They react with dilute acids to liberate hydrogen gas.



Uses:

(1) Mischemetal:

Composition: 50% Cerium, 40% Lanthanum and other Lanthanoids, 5% iron, traces of S,C,Ca and Al.

It is used in making magnesium-based alloy. Because of its pyrophoric nature (tendency to emit spark when struck), it is employed in production of bullets, shells and flints.

(2) Their oxides are used for making UV protective lenses.

(3) Ceric sulphate is a well-known oxidising agent.

Lecture - 54

THE ACTINOIDS :

As mentioned earlier, Actinoids are radioactive. The earlier members of the series have relatively long half-lives and the later ones have half-lives ranging from a day to 3 minutes for Lawrencium.

(i) Electronic Configuration:

The general electronic configuration of Actinoids is $7s^2\ 6d^{0-1}\ 5f^{1-14}$ (Table 2). The actinoids have their stable configuration for f^0, f^7 and f^{14} occupancy. So there is certain irregularity in their electronic configuration.

Ex: Am–[Rn] $7s^2 5f^7$

Cm–[Rn] $7s^2 6d^1 5f^7$

The 5f orbitals are not as buried as 4f orbitals. So they can participate in bonding to a greater extent.

Table 2 : Some properties ofAcitinium and Actinoids

Aotmic			Electronic congiguration			Raddi/pm	
Number	Name	Symbol	M	M^{3+}	M^{4+}	M^{3+}	M^{4+}
89	Actinium	Ac	$6d^17s^2$	$5f^0$		111	
90	Thorium	Th	$6d^27s^2$	$5f^1$	$5f^0$		99
91	Protactinium	Pa	$5f^26d^17s^2$	$5f^2$	$5f^1$		96
92	Uranium	U	$5f^36d^17s^2$	$5f^3$	$5f^2$	103	93
93	Neptunium	Np	$5f^46d^17s^2$	$5f^4$	$5f^3$	101	92
94	Plutonium	Pu	$5f^67s^2$	$5f^5$	$5f^4$	100	90
95	Americium	Am	$5f^77s^2$	$5f^6$	$5f^5$	99	89
96	Curium	Cm	$5f^76d^17s^2$	$5f^7$	$5f^6$	99	88
97	Berkelium	Bk	$5f^97s^2$	$5f^8$	$5f^7$	98	87
98	Californium	Cf	$5f^{10}7s^2$	$5f^9$	$5f^8$	98	86
99	Einstenium	Es	$5f^{11}7s^2$	$5f^{10}$	$5f^9$	-	-
100	Fermium	Fm	$5f^{12}7s^2$	$5f^{11}$	$5f^{10}$		
101	Mendelevium	Md	$5f^{13}7s^2$	$5f^{12}$	$5f^{11}$	-	-
102	Nobelium	No	$5f^{14}7s^2$	$5f^{13}$	$5f^{12}$	-	-
103	Lawrencium	Lr	$5f^{14}6d^17s^2$	$5f^{14}$	$5f^{13}$	-	-

Oxidation states :

The 5f, 6d and 7s subshells are of comparable energies. So the actinoids show a greater range of oxidation states (Table-3).

Table 3 : Oxidation states of Actinium and Actinoids

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3		3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4	4						
		5	5	5	5	5								
			6	6	6	6								
				7	7									

However, like lanthanoids the +3 oxidation state is common to all of them. As evident from the table the oxidation state of actinoids increases upto the middle of the series and then decreases for the succeeding elements. This is because the 5f, 6d and 7s subshells are of comparable energies and all their electrons can take part in bond formation.

(iii) Ionic sizes :

The actinoids also show **"actinoid contraction"** (like lanthanoids) due to the poor shielding effect of '5f subshells. As a result, the radii of these atoms or ions (decrease across the series. (Table 2)

(IV) General characteristics of Actinoids :

1. The actinoid metals are all silvery in appearance.
2. **Structure :** The actinoids display a variety of structures due to irregularities in metallic radii.
3. **Colour:** The actinoid cations are coloured due to f-f transition. Those ions having no 5f-electron or seven 5f-elecrons (i.e. exactly half-filled f-subshell) are colourless.

Ex:	Ac^{2+}	$5f^0$ colourless	Am^{3+}	$5f^0$ pink
	U^{3+}	$5f^3$ red	Cm^{3+}	$5f^7$ colourless
	Np^{3+}	$5f^4$ blue	Th^{3+}	$5f^0$ colourless
	Pu^{3+}	$5f^5$ violet	etc.	

4. **Melting and Boiling points :** Actinoids have high melting and boiling points. But they do not show any regular trend.
5. **Density :** They have high densities.
6. **Ionization enthalpies :** The actinoids have lower ionization enthalpies than lanthanoids because ‘5f is less penetrating than ‘4f and hence is more effectively shielded from nuclear charge.
7. **Electropositive character :** Actinoids are highly electropositive like the Lanthanoids.
8. **Magnetic behaviour :** The actinoids are strongly paramagnetic. The magnetic susceptibility of actinoids are higher than the lanthanoids.
9. **Chemical behaviour:**
   (a) Actinoids react with boiling water to give oxides and hydroxides.
   (b) They react with most of the non-metals at moderate temperature.
   (c) They are rendered passive by action of nitric acid.

Uses of Actinoids :

(1) Thorium: It is used as a nuclear fuel, anti-carcinogen and for manufacture of mantles of incandescent lamps.

(2) Uranium : It is used as nuclear fuel, textiles, ceramics, medicines and to impart colour (green) to bulbs.

(3) Plutonium : It is used in nuclear reactors and manufacture of atomic bombs.

COMPARISON BETWEEN LANTHANOIDS AND ACTINOIDS :

Though Lanthanoids and Actinoids resemble each other in certain properties there are also some dissimilarities between them.

Similarities:

(1) +3 oxidation state is common for both the series of elements.

(2) Both are electropositive and have low value of ionisation Enthalpy $\left(\Delta_i H\right)$.

(3) Both exhibit magnetic and spectral properties.

(4) Lanthanoids show ‘Lanthanoid contraction’ and Actinoids show ‘Actinoid contraction’.

Differences:

(1)	They are non-radioactive. Exception-Promethium.	(1)	They are radioactive.
(2)	Besides +3 oxidation state they show +2 and +4 oxidation states only in a few cases,	(2)	They show higher oxidation states +4, +5, +6, +7 besides +3 oxidation state
(3)	Do not form oxocation.	(3)	UO_2^+, UO_2^{2+} PuO_2^{2-} oxocation are formed by them.
(4)	Lanthamides compounds are less basic	(4)	More basic
(5)	Most of the ions are colourless.	(5)	Most of the ions are coloured.

HOME ASSIGNMENT

1. **(a)** Explain the following :

(i) $La(OH)_3$ is more basic than $Lu(OH)_3$.

(ii) Zr & Hf exhibit similar properties.

(iii) Ce(III) Z=58 can easily oxidised to Ce(IV)

(iv) Actinoid contraction is greater from element to element than lathanoid contraction.

(v) La^{3+} and Lu^{3+} are colourless. Wheres Sn^{3+} and Eu^{3+} are coloured.

(b) What is lanthanide contraction ? Discuss its effect in periodic table.

(c) Why is separation of Lanthanoids element difficult ? How are these isolate?

(d) Fill in the gaps :

(i) The general electron configuration of Lanthanoids is ________ .

(ii) The common oxidation state of Lanthanoids is _______ .

(iii) Lanthanide ions are coloured due to ______ transition.

Lecture - 55-61

UNIT - IX

CO-ORDINATION COMPOUND

DOUBLE SALTS :

The compounds which when dissolved in water or any other solvent decompose into their constituent compounds and which exist only in crystal lattices are known as **double salts.** The physical and chemical properties of these compounds are almost the same as those of individual compounds.

Examples include

(i) $Al_2 (SO_4)_3 . K_3SO_4 .24H_2O$ (Potash Alum)

(ii) $FeSO_4 . (NH_4)_2SO_4 . 6H_2O$ (Mohr's salt)

(iii) $KCl. MgCl_2 .6H_2O$ (Carnallite)

So a solution of potash ahmi shows the same physical and chemical properties **as** a mixture of solutions of Aluminium sulphate and Potassium sulphate.

CO-ORDINATION COMPOUNDS :

The compounds which when dissolved in water or any other solvent lose the identity of ions or molecules are known as **co-ordination compounds.** The physical and chemical properties of these compounds are completely different from those of the constituents. Some common examples are

(i) $[Co(NH_3)_6]Cl_3$ – Hexaamminecobalt (III) chloride

(ii) $K_4[Fe (CN)_6]$ – Potassium hexacyanidoferrate (II)

(iii) $[Ni(NH_3)_6]Cl_2$ –Hexaamminenickel (II) chloride

Hexaamminenickel (II) chloride ionises in solution as

$$[Ni(NH_3)_6] \rightleftharpoons \left[Ni\left(NH_3\right)_6\right]^{2+} + 2Cl^-$$

On evaporating the solution, the compound can be recovered. The compound in solution does not show the properties of Ni^{2+} ions or ammonia molecules.

Difference between double salt and complex salt

	Double salt		**Complex salt**
(i)	Equimolar solution of two simple salts	(i)	May or may not be equimolar.
(ii)	Disociate complete into ions.	(ii)	Complex ions never dissociate
(iii)	Ionic compounds without dative bond	(iii)	Complex part contains dative bonds so ions in it loses its identity e.g. CN^- in ferrocyamide.

DEFINITIONS OF SOME IMPORTANT TERMS :

(i) Coordination Complex and Complex ions

Two or more stable chemical species combine to form a compound known as Co-ordination complex. The compound retains its identity both in the solid as well as in dissolved state.

e.g. $CuSO_4$ and NH_3 are two stable chemical species and they combine to form a coordination complex $[Cu(NH_3)_4]SO_4$.

A water-soluble co-ordination compound invariably contains a complex ion. For example, $[Cu(NH_3)_4]SO_4$ contains $[CuNH_3)_4]^{2+}$ complex ion and $K[Ag(CN)_2]$ contains the complex ion $[Ag(CN)_2]^-$. A complex ion is thus electrically charged ion which contains a central metal atom or ion surrounded by a group of ions or neutral molecules. So $[Cu(NH_3)_4]^{2+}$ contains a central ion Cu^{2+} surrounded by four ammonia molecules (neutral).

(ii) **Central ion**

The ion to which a fixed number of ions or neutral molecules are bound in a definite geometrical arrangement around it is known as the **central ion.** For example, in complex ion $[Ni(NH_3)_6]^{2+}$, Ni^{2+} is the central ion and in $[Fe(CN_6]^{3-}$, Fe^{3+} is the central ion. The central ion is a Lewis acid. $[Ni(CO)_4]$, here central metal is an atom.

(iii) Ligands

The ions or molecules bound to the centra! ion in the coordination compounds, are called ligands. For example, in complex ions $[Ni(NH_3)_6]^{2+}$ and $[Fe(CN_6)\ ]^{3-}$ the ligands are molecules of ammonia and cyanide ions respectively. The ligands may be simple ions like Cl^-, small molecules like H_2O and NH_3, larger molecules like $H_2NCH_2CH_2NH_2$ or $N(CH_2CH_2NH_2)_3$ or even macromolecules like proteins.

(iv) Coordination Number

The ligands are attached to the central ion through coordinate bonds. The number of ligands attached to the central ion is known as the coordination number of that ion. For example, co-ordination number of Ag^+ in $[Ag(CN)_2]^-$ is 2. Co-ordination number of Cu^{2+} in $[Cu(NH_3)_4]^{2+}$ is 4. The most common coordination numbers are 2,4, and 6.

(v) Coordination sphere

The central ion bonded to the ligands constitute the **co-ordination sphere.** The co-ordination sphere is written within the square bracket.

e.g.$[Ag(CN)_2]^-$

Types of Ligands

A ligand necessarily contains one or more donor atoms for co-ordination with the central ion or atom. On the basis of number of donor atoms the ligands may be classified as follows :

(1) Unidentate or monodentate ligands

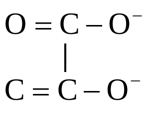
The ligands which can coordinate to the central ion through only one donor atom are known as **unidentate** or **monodentate** ligands. The common examples are-

H_2O, Cl^-, NH_3, OH^-, NO_2^- etc.

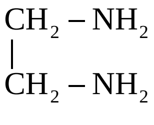
(2) Bidentate or didentate ligands

The ligands which can coordinate to the central ion through two donor atoms are called **bidentate** or **didentate** ligands.

The examples are



$$\begin{array}{c} O=C-O^- \\ | \\ C=C-O^- \end{array}$$

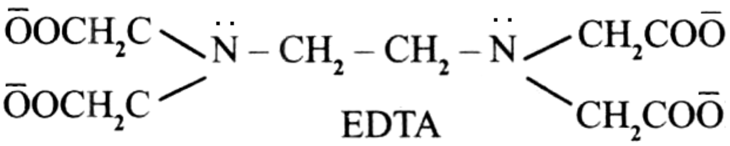


$$\begin{array}{l} CH_2-NH_2 \\ | \\ CH_2-NH_2 \end{array}$$

(3) Polydentate ligands

The ligands which can co-ordinate to the central ion through more than two donor atoms are called **polydentate** ligands. They may be **tridentate, tetrandentate. pentadentate** and **hexadentate** depending upon the number of donor atoms as 3, 4, 5, and 6 respectively.

e.g. Ethylene diamine tetracetate acid (EDTA) is an important hexadentate ligand. It binds through two nitrogen and four oxygen atoms of four $-COO^-$ groups to the central metal ion.

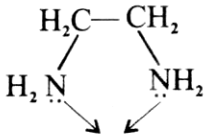


EDTA

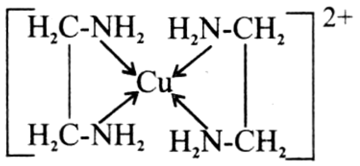
(4) Chelating ligands and Chelates

A bidentate or polydentate ligand may link to central metal ion through two or more donor atoms forming a ring structure. The ligand is called a **chelating ligand** and the complex is called a **chelate.**

For example, ethylene diamine (a bidentate ligand) coordinates through both the Nitrogen atoms to central Cu^{2+} ion forming a ring structure.



Ethylene diamine
Bidentate ligand
acting as chelating ligand



Chelate cation

WERNER'S CO-ORDINATION THEORY:

To explain the formation and structure of complex compounds **Werner** in 1823 put forward the theory of coordination for which he was awarded Nobel prize in chemistry. He is known as the the father of coordination chemistry.

Postulates

(1) Metal atoms in coordination compounds exhibit two types of valencies (a) **Primary valency** (b) **Secondary** valency. The primary valency is non-directional and ionisable. It corresponds to oxidation state. The secondary valency is directional and non-ionisable. It corresponds to coordination number.

(2) Each metal atom exhibits a fixed number of **secondary valencies** i.e. it has a fixed coordination number.

e.g. C.N. of Ag^+, Cu^{2+}, Fe^{3+}, 2, 4, 6 respectively.

(3) The primary valencies are satisfied by negative ions whereas the secondary valencies are satisfied either by negative ions or by neutral molecules.

(4) The secondary valencies are responsible for imparting a particular geometry to the coordination compound. For example, if the central metal ion has four secondary valencies, then they form either a tetrahedral or square planar arrangement around the central metal ion. If the central metal ion has six secondary valencies, then these are arranged octahedrally around the metal ion. In otherwords the **stereochemistry** of the complex is determined by the **secondary** valencies.

Explanation of Structure of complexes on the basis ofWerner's theory

The structures of various cobalt ammines may be explained by Wemer's theory. In all such compounds cobalt exhibits a primary valency of three and secondary valency of six. The primary valencies are represented by dotted lines whereas the secondary valencies by thick lines in thefollowing figures.

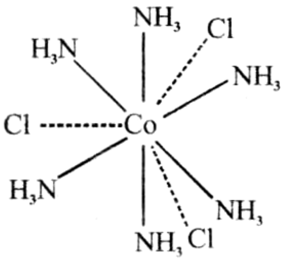


Fig. 1 Structure of $COCl_3.6NH_3$ complex

(a) Total no. of ions = 4
(3 numbers of Cl^- ion,
1 complex ion $[Co(NH_3)_6]^{3+}$)

(b) The complex = $[Co(NH_3)_6]Cl_3$

(c) The number of Cl^- ions getting precipitated on addition of $AgNO_3$ =3

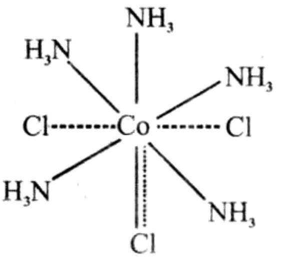


Fig. 2 Structure of $CoCl_3.5NH_3$ complex

(a) Total number of ions = 3
(2 numbers of Cl^- ion,
1 complex ion)

(b) The complex - $[CoCl (NH_3]Cl_2$

(c) The number of Cl^- ions getting precipitated on addition of Ag NO_3=2

(d) One Cl ion exhibits a dual character. It is held by a secondary as well as a primary valency,

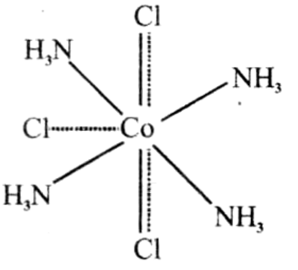


Fig : 3 : Structure of $CoCl_3.4NH_3$ complex

(a) Total no. of ions =2
(one Cl~ ion), one complex ion

(b) The complex $[CoCl_2 (NH_3)_4]Cl$

(c) The number of Cl^- ion getting precipitated on addition of $AgNO_3$=1

(d) Two number of Cl^- ions are held by primary as well as secondary valencies.

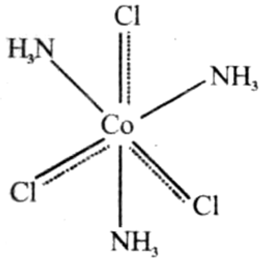


Fig : 4 : Structure of $CoCl_3.3NH_3$ complex

(a) Total number of ions =zero.
It is a neutral molecule.

(b) The complex $[CoCl_3 (NH_3)_3]$

(c) The number of Cl^- ions getting precipitated on addition of $AgNO_3$= nil, Non conducting.

(d) Three numbers of Cl^- ions are held by primary **as well** as secondary valencies

NOMENCLATURE OF COORDINATION COMPOUNDS: IUPAC SYSTEM :

Basic rule :

I. **Order of naming** ions: In ionic complexes, the cation is named first and then the anion. For example:

$[Ni(NH_3)_6]Cl_2$is named as Hexaamminenickel (II) chloride.

$[Cr(NH_3)_6\,](NO_3)_3$ is named as Hexaamminechromhmi (III) nitrate.

and $K_2[PtCl_6]$, as Potassium hexachloridoplatinate (IV).

II. **Non-ionic complexes:** They are given one-word name.

For example: $[Pt(NH_3)_2Cl_4]$ is named as Diamminetetrachlorid oplatinum (IV)

$[Co(NH_3)_3(NO_7)_3]$ is named as Triamminetrinitrocobalt(III).

III. **Naming the complex:**

i) When the name of the complex is written, the ligands are written in alphabetical order regardless of their charge, followed by the metal.

For example: $[Pt.Cl.NO_2(NH_3)_4]SO_4$ is named as Tetraammine-chloridonitroplatinum(IV) sulfate.

ii) When the formula of the complex is written, the complex ion should be enclosed in square brackets. The metal is written first, then the coordinated groups are listed in the order- negative ligands, neutral ligands, positive ligands (and alphabetically according to the first symbol within each group).

(a) The name of the negative ligands end in ‘o’.

Thus,

F^-	fluoroido	H^-	hydrido	HS^-	mercapto	NO_2^-	nitro
Cl^-	chlorido	OH^-	hydroxido	S^{2-}	sulfido	CH_3COO^-	acetato
Br	bromido	O^{2-}	oxido	SO_4^{2-}	sulphato	$S_2O_3^{2-}$	thiosulphato
I^-	iodido	O_2^{2-}	peroxido	CN^-	cyanide	NO_3^-	nitrato

(b) Neutral ligands are named as the molecule. Thus, water (H_2O) is named as aqua, ammonia (NH_3) as ammine, CO as carbonyl and NO as nitrosyl. The ligands N_2 is called dinitrogen and O_2 is called dioxygen. Organic ligands are given their common names as phenyl, methyl, ethylenediamine (shortly as ‘en’), pyridine (shortly as ‘py’) glycine (Gly), dimethyl glyoxime (DMG) etc.

(c) Positive ligands end in ‘ium’ For example, $NH_2 - N^+H_3$ is named as hydrazinium. (But when NO^+ ligand is used, it is called nitroso), N^+O_2 nitronium.

IV) Prefixes to indicate number of ligands: When there are several simple ligands of the same kind, their number is indicated by di, tri, tetra, penta and hexa. If the ligands have complex names, to avoid confusion bis, tris, tetrakis are used instead of di, tri and tetra and the name of the ligand is kept within brackets. For example- $K_3[Al(C_2O_4)_3]$ is named as Potassium trioxalatoaluminate (III) and $[CoCl_2(NH_2CH_2CH_2NH_2)_2]_2SO_4$ or $[COCl_2(en)_2]_2SO_4$ is named as Dichlorobis (ethylene diammine) cobalt(lll) sulphate.

V) **Oxidation state of central metal** is shown by Roman numerals (I, II, III etc) in brackets immediately following its name. For zero oxidation state,

(0) is written.$[Ni(CO)_4]$, Tetracarbonyl nickel (O)

VI) Ending of names: The complex negative ions end in ‘ate’.

For example: $K_4[Fe(CN)_6]$ is named as Potassium hexacyanido ferrate (II)

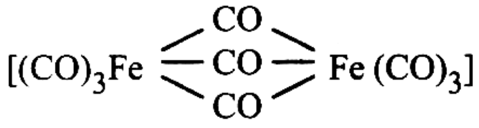
and $K_3[Fe(CN)_6]$ is Potassium hexacyanidoferrate (III).

$K[PtCl_5(NH_3)]$ is named as Potassium amminepenta-chloride platinate(IV)

and $[Co(NO_2)_3(NH_3)_3]$ as Triamminetrinitrocobalt(III).

VII) **Bridging groups:** Ligands which link two centres of coordination are usually separated from the rest of the complex by a ‘’hyphen’ (–) and are denoted by the prefix μ . If there are two or more bridging groups of the same kind, this is indicated by di -μ -, tri -μ - etc. Bridging groups are listed alphabetically with other groups unless the symmetry of the molecule allows a simpler name.

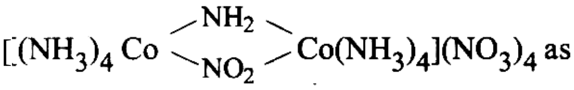
For Example: $[(NH_3)_5Co.NH_2.Co(NH_3)_5]\ (NO_3)_5$ is named as μ - Amidobis [pentaamminecobalt (III)] nitrate,



$[(CO)_3Fe(CO)_3Fe(CO)_3]$

as Tri–μ-carbonyl-bis (tricarbonyl iron(0))

and

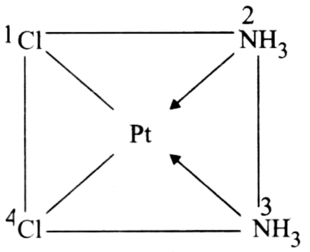


$[(NH_3)_4Co(NH_2)(NO_2)Co(NH_3)_4](NO_3)_4$

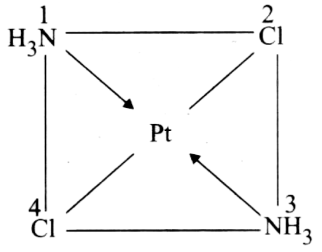
as μ- Amido -μ - nitrobis [tetraamminecobalt (III)] nitrate.

VIII) Sometimes a ligand may be attached through different atoms. Thus, M-NO_2 is called nitro whereas M-ONO is called nitrito. Similarly, M-SCN in called thiocyanato and M-NCS is called isothiocyanato. Systematically they are named as thiocyanato-S or thiocyanato-N to indicate which atom is bonded to the metal. This convention is extended to other cases where the mode of linkage is ambiguous. For example, $NH_4[Cr(NCS)_4(NH_3)_3]_2$ is named as Ammonium diamminethiocyanato-N-chromate (III) and $[Cd(SCN)_4]SO_4$ as Tetrathiocyanato-S-cadmium (II) sulphate. Such ligands are called ambidentate ligands.

IX) **Naming Geometrical isomers:-** Geometrical isomers are named by the use of cis to indicate the adjacent positions of two similar ligands and trans to indicate the opposite. For a square planar complex such as $[Pt(NH_3)_2Cl_2]$ which is isolated in two forms cis and trans can be shown as



cis (1,4 or 2,3 positions are *cis*)



trans (1,3 or 2,4 positions are *trans*)

X) **Naming optical isomers:-** Dextro and-leavs rotatory optically active complex compounds are designated as(+) and (-) or as d- and *l*- respectively.

A few IUPAC names are given below with their formulae.

$\left[Co(NH_3)_6\right]Cl_3$	Hexaamminecobalt (III) chloride
$\left[CoCl(NH_3)_5\right]^{2+}$	Pentaamminechloridocobalt (III) ion.
$\left[Co.Cl.CN.NO_2(NH_3)_3\right]$	Triamminechloridecyanidonitrocobalt (III).
$\left[Co.SO_4(NH_3)_4\right]NO_3$	Tetraamminesulphatocobalt(III) nitrate.
$K_3\left[Fe(CN)_6\right]$	Potassium hexacyanidoferrate(III).
$K_3\left[Fe(CN)_5\ NO\right]$	Potassium pentacyanidonitrosylferrate(II) (Here, NO is neutral)
$K_2\left[\overset{+6}{Cr}(CN)_2^{-2}(O)_2^{-4}(O_2)^{2-}\ NH_3\right]$	Potassium amminedicyanidodioxidoperoxidochromate(VI).
$Na_3[Ag(S_2O_3)_2]$	Sodium bis(thiosulphato)argentate(I).
$\overset{+2}{Na}_2\left[\overset{+2}{Fe}(CN)_5^{-5}\ \overset{+1}{NO}\right]$	Sodium pentacyanidonitrosoniumferrate(II) (Here, NO is NO^+) (Sodium nitroprusside)
$\left[Fe(H_2O)_5\ NO\right]SO_4$	Pentaaquanitrosoniumiron(I) sulphate (Here, NO is NO^+) (This complex is formed during brown-ring test for nitrate)
K_2HgI_4	Potassium tetraiodido hydragyrate (II)
$LiAlH_4$	Lithium tetrahydridoaluminate(III)

HOME ASSIGNMENT

Name the follows compounds

(i) $\left[CuCl_2(CH_3NH_2)_2\right]$

(ii) $\left[Pt(py)_4\right]\left[PtCl_4\right]$

(iii) $\left[Cr(NH_3)_6\right]\left[Co(C_2O_4)_3\right]$

(iv) $\left[Pt(NO_2)(NH_3)(C_5H_5N)(H_2O)\right]Cl$

(v) $\left[Cr(H_2O)_4Cl_2\right]Cl.2H_2O$

(vi) $K_2[Cu(CN)_4]$

(vii) Ni $(DMG)_2$

(viii) $Fe(CO)_5$

(ix) $Fe_4\left[Fe(CN)_6\right]_3$

(x) $K_4\left[Ni(CN)_4\right]$

Lecture - 58

ISOMERISM IN COORDINATION COMPOUNDS :

Compounds which have the same chemical composition but different arrangements of their atoms are called **isomers** and this phenomenon is known as isomerism. The isomers differ in one or more physical or chemical properties.

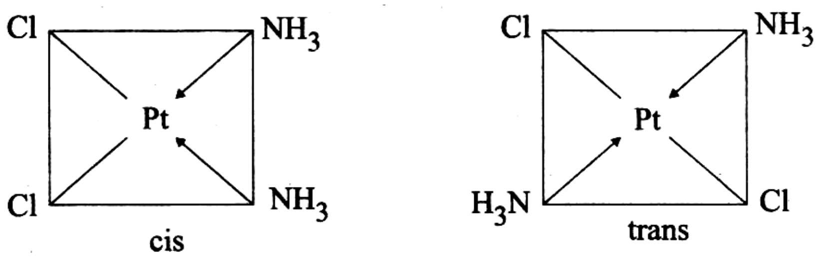
Metal complexes exhibit different kinds of isomerism. The main types are (a) Stereoisomerism and (b) Structural asomerism Steroisomerism is further subdivided into

(I) **Geometrical isomerism** (II) Optical isomerism. **Stereoisomers** have **the** same **chemical** formula and chemical bonds, but they have **different** spatial arrangements. Structural isomers have different bonds.

(I) **Geometrical isomerism —**

Coordination Number 4 — In these complexes two principal geometries are found i.e. **tetrahedral** and **square planar.** Cis-trans isomerism is not possible in tetrahedral complexes. However, cis-trans isomerism is very common amongst square planar complexes.

In complexes of type Ma_2b_2 such as $[PtCNH_3)_2Cl_2]$ or $[Pd(NH_3)_2(NO_2)_2]$ cis-trans isomers are found. Similar complexes of Ni(II), Cu (II) and Co(II) are also known

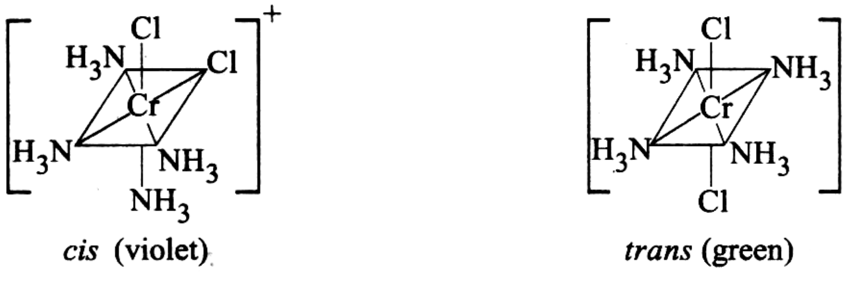


(Ligands adjacent to each other) **(Ligands opposite i.e. at a distance of 180^0)**

Cis-trans forms of $[Pt(NH_3)_2Cl_2]$

In complexes of type Ma_2bc where M = Pt, a = NH_3 and b, c = Cl^-, Br^-, NO_2^- , SCN^- etc. cis-trans isomers exist Mobed form three isomers.

Coordination Number 6 — The regular geometric arrangement is octahedral. Tetraammine dichloridochromium(III) ion exists as cis (violet) and trans (green) forms.



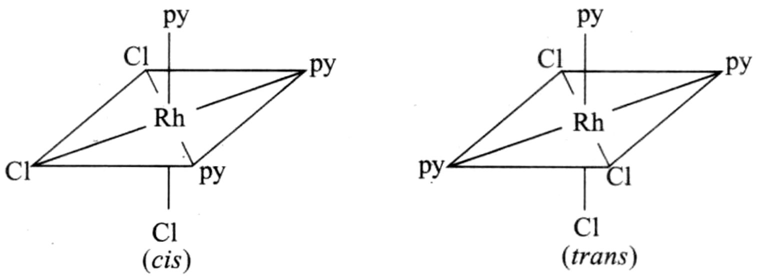
(Angular distance 90^0) (Angular distance 180^0)

Cis-trans forms of $[Cr(NH_3)_4Cl_2]^+$

Large number of octahedral complexes of the type Ma_4b_2 or Ma_2b_4 or Ma_4xy where M=Co(III), Cr (III), Rh (III) and Pt (IV) exist as isomers.

Complexes of the type Ma_3b_3 exist in two isomeric forms.

For example: $[Rh(py)_3Cl_3]$, where py = pyridine.



Facial

Mobcde ⇒ 15 different geometrical isomers.

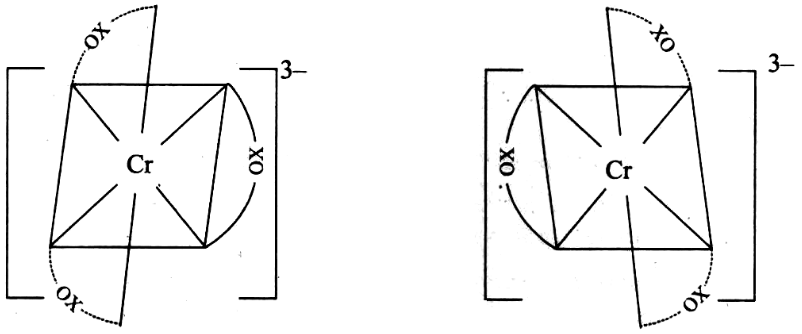
meridional

$[Co(en)_2Cl_2]^+$ exhibit geometrical isomerism.

Cis-trans forms of $[Rh(py)_3Cl_3]$

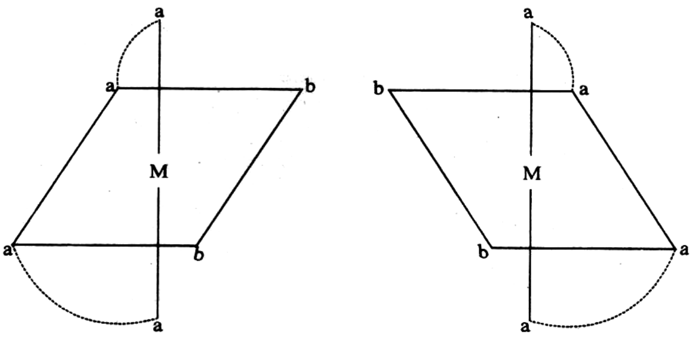
(II) **Optical isomerism** — Optical activity is due to lack of symmetry of the molecule. It is known that d- and *l*- isomers are just mirror images of one another just as the left hand is the mirror image of the right hand. Optical isotners have identical chemical and physical properties and differ only in the direction in which they rotate the plane of polarised light. The dextro form rotates the plane towards the right and laevo form, towards the left. **Only** tetrahedral complexes (coordination number-4), containing two unsymmertrical bidentate ligands of Be (II), B (III) and Zn (II) can be resolved into optically active forms. Square planar complexes are seldom optically active.

Coordination Number 6 — Common examples are compounds or ions of the type $[M(aa)_2]$ whose aa = bidentate ligand (occupies two coordination positions). For example, trioxalatochromate (III) ion exists in two optically active forms.



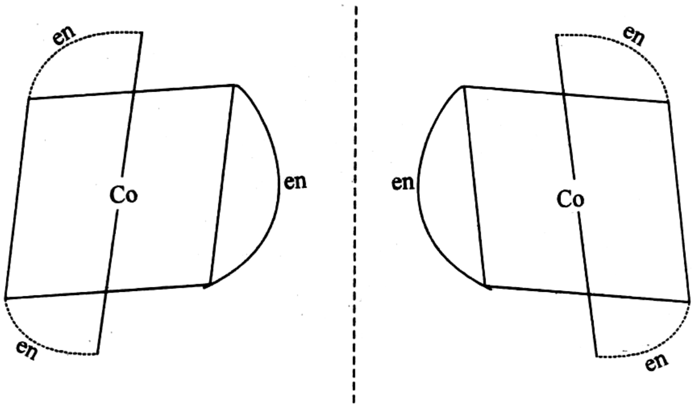
Optical isomers of trioxalatochromate (III) ion

Some other common complexes with coordination number 6, belong to the type $[M(aa)_2b_2]$ where 'aa' = bidentate ligand. The cis-form of these complexes have been resolved into d- and *l*-isomers but the trans-form does not show optical isomerism.



d- and *1*-isomers of cis-form of the complex $[M(aa)_2b_2]$

An example of this type is the *cis*-form of dichloro bis (ethylenediamine) rhodium (III). Also complexes of the type $[M(aa)_3]$ where 'aa' = bidentate ligand, for example, tris(ethylenediamine) cobalt (III) cation gives the d-and *I*-isomers.



d– and *l*-isomers of tris (ethylenediamine) cobalt(III).

Structural isomerism :

Types 1) Ionisation isomerism — This type of isomerism is shown by such compounds which have same composition but liberate different ions in solution. In such isomers, the position of groups whithin or outside the coordination sphere differs.

Examples:	$[Co(NH_3)_5SO_4]Br$ (Red	-	liberates Br^- ions in solution.
	and		
	$[Co(NH_3)_5Br]SO_4$(purple)	-	liberates SO_4^{2-} ions in solution.

2) **Hydrate isomerism —** This type of isomerism results from the replacement of a coordinated group by water of hydration. These isomers differ widely in their physical and chemical properties.

Examples :	$[Cr(H_2O)_6]Cl_3$ (Violet)	-	Does not lose water molecules but three Cl^- ions are precipitated by $AgNO_3$ solution.
	$[Cr(H_2O)_5Cl]Cl_2(H_2O)$(Light green)	-	Loses one molecule of water but two Cl^- ions are precipitated by $AgNO_3$ solution.

$[Cr(H_2O)_4Cl_2]Cl(2H_2O)$(Dark green)- Loses two molecules of water on dehydration, but one Cl^- ion is precipitated by $AgNO_3$ solution.

3) **Linkage isomerism** — This type of isomerism is shown by such complexes which contain a monodentate ligand having more than one donor atom. (ambidentate ligand) Thus, cyanide ion : $C{\equiv}N^-$: can attach itself to metal M either through the carbon $M-C{\equiv}N^-$: or the nitrogen $M{-}N{\equiv}C^-$: Similarly, $:N \equiv C{-}S^-$: (through N or S), $:C{\equiv}O$: (through C or O).

4) **Coordination isomerism**— This type of isomerism is shown by such compounds which contain both cationic and anionic complex species and it results from random distribution of ligands.

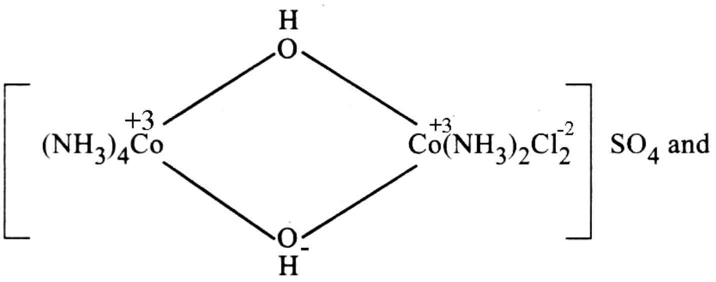
Example : $[Co(NH_3)_6]\,[Cr(CN)_6]$ and $[Cr(NH_3)_6]\,[Co(CN)_6]$

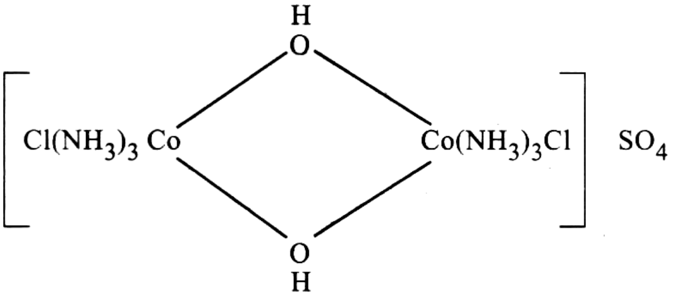
5) **Ligand isomerism —** When isomeric ligands are associated into complexes, the complexes are isomers of each other.

Example: $[Co(pn)_2Cl_2]^+$ and $[Co(tn)_2Cl_2]^+$

pn= 1,2- diaminopropane, to = 1, 3 - diaminopropane

6) Coordination position isomerism— This type of isomerism is shown by bridged complexes and involve different placement (attachment) of ligands. It is a special type of coordination isomerism.





BONDING IN COORDINATION COMPOUNDS :

Limitations of Werner theory :

(a) Why the coordination compounds are formed by only certain elements ?

(b) Why the bonds present in coordination compounds have directional properties?

(c) Why certain coordination compounds appear coloured and they possess characteristic magnetic and optical properties ?

Present theory is to explain the bonding in complexes.

(a) The Valence Bond Theory
(b) The Crystal Field Theory
(c) The Molecular Orbital Theory

THE VALENCE BOND THEORY (PAULING)

Postulates :

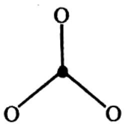
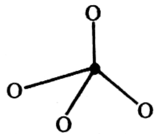
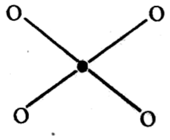
1. During the formation of coordination compounds the ligands coordinate with the central metal ion. For the formation of coordinate bond the central metal ion provides an adequate number of empty orbitals to accomodate the electron pairs from the ligand. The number of empty orbitals is equal to the coordination number of the central ion / atom.

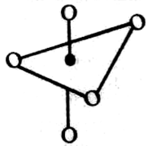
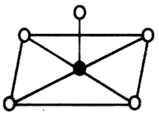
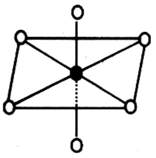
2. The atomic orbitals (s,p and d) of the metal hybridise giving hybrid orbitals of equivalent energies. The number of hybridising orbitals is equal to the number of hybrid orbitals. The hybrid orbitals are directed to the positions of the ligand depending upon the geometry of the complex. (see Table-1)

3. Each ligand must have atleast one orbital containing a lone pair of electrons.
4. The inner (*d*-orbitals i.e. (n-1)d or the outer d-orbitals i.e. n d- orbitals participate in hybridisation. For example, in case of octahedral structure the hybridisation is of (n-1) d^2sp^3 type or n sp^3d^2 type. The complexes thus formed are known as low spin (inner orbital complex)and high spin (outer orbital complexes) respectively.

5. The ligand -metal coordinate bond is formed by the overlapping of vacant hybrid orbitals of metal ion with completely filled orbitals of the ligand. The number of such bonds varies with the number of vacant orbitals made available by the central metal ion/atom.

Table - 1

Coordination number	Hybrid orbitals	Molecular geometry	Examples
2	*sp*	 Linear	$Ag(NH_3)_2^+$, $Ag(CN)_2^-$
3	*sp²*	 Trigonal planar	$[HgI_3]^-$
4	*sp³*	 Tetrahedral	$[Ni(CO)_4]$, $[Zn(NH_3)_4]^{2+}$
4	*dsp²* The *d*-orbital involved in $d_{x^2-y^2}$ of the inner i.e (n–1)th shell.	 Square planar	$[Ni(CN)_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$

5	*dsp³* The *d*-orbital involved i.e. d_{z^2} of the inner i.e. (n–1)th shell.	 Trigonal bipyramidal	[Fe(CO)$_5$]
6	*sp³d* The *d*-orbitals involved i.e. $d_{x^2-y^2}$ of the outer i.e. nth shell	 Square pyramidal	[SbF$_5$]$^{2-}$
7	*d²sp³* or *sp³d²* The *d* orbitals involved are $d_{x^2-y^2}$ and d_{z^2} of the inner in (n–1)th shell in the 1st case and of the outer i.e. nth shell in the second case	 Octahedral	[Co(NH$_3$)$_6$]$^{2+}$ (n-1)*d* orbitals are involved. **(inner orbital complex)** [CoF$_6$]$^{3-}$ n*d* orbitals are involved. **(outer orbital complex)**

The stereochemical and magnetic properties of co-ordination compounds can be predicted by Valence bond theory. We know that the substance which contains no unpaired electron is known as **diamagnetic** substance and it is repelled by the magnetic field. On the other hand, the substance which contains unpaired electron is known as **paramagnetic** substance and it is attracted by the magnetic field. It is possible to predict the geometry of the complex, the number of unpaired electrons and the type of hybridisation involved on the basis of Valence bond theory.

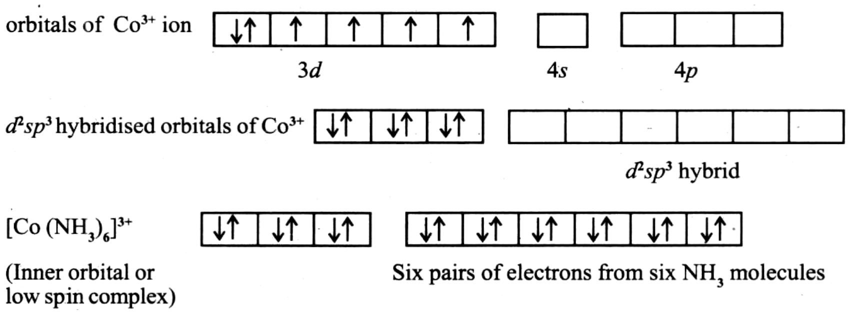
Examples of Octahedral complexes

Consider the formation of complexes of Co (III) on the basis of Valence bond theory.

1. Hexaamniinecobalt(III) ion, [Co(NH$_3$)$_6$]$^{3+}$

The outer electronic configuration of Co (III) is 3d^6. The six electrons are to be distributed among the five numbers of 3d orbitals. The hybridisation scheme is as shown below in the diagram.

Co(Z=27) 3d^{7}4s^2



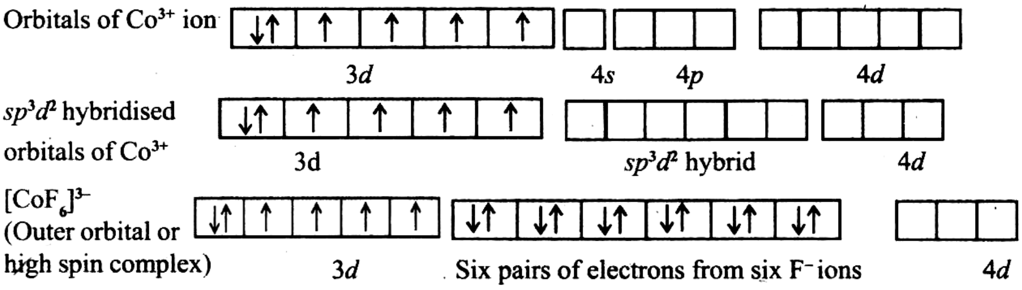
Formation of octahedral complex [Co(NH$_3$)$_6$]$^{3+}$ involving d^{2}sp^3 hybridisation of Co^{3+} ion orbitals

The six number of hybrid orbitals are occupied by six pairs of electrons one from each NH_3 molecule. The complex has octahedral geometry and because of absence of unpaired electrons it is diamagnetic in nature . In the formation of this complex the inner orbital 3d is used in hybridisation. Hence the complex is known as inner orbital or low spin or spin paired complex.

2. Hexafluoridocabalt (III) ion, $[CoF_6]^{3-}$

Hexafluoridocobalt (III) ion is paramagnetic. In this case the 3d orbitals do not take part in hybridisation, rather the 4d orbitals are involved. The hybridisation scheme is as shown below in diagram.

Co(III) $3d^6\ 4s^0\ 4p^0\ 4d^0$



Formation of octahedral $[CoF_6]^{3-}$ complex involving sp^3d^2 hybridisation of Co^{3+} ion orbitals

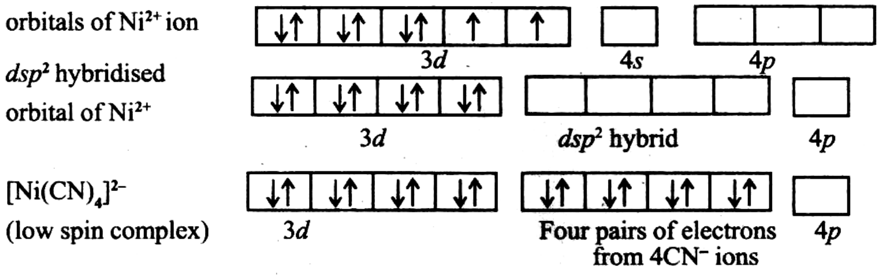
This is outer orbital high spin complex, (n=4). (F^- ligand is a weaker ligand). Complex is highly paramagnetic.

Examples of Square planar and Tetrahedral complexes

(i) Tetracyanidonickelate (II) ion, $|Ni(CN)_4]^{2-}$

The Ni (II) ion has 3d” outer electronic configuration. The 8 electrons are to be distributed in five d orbitals. According to Hund’s rule, there are two unpaired electrons. The hybridisation scheme is as show below in diagram.

$_{28}Ni\ 3d^8\ 4s^2$

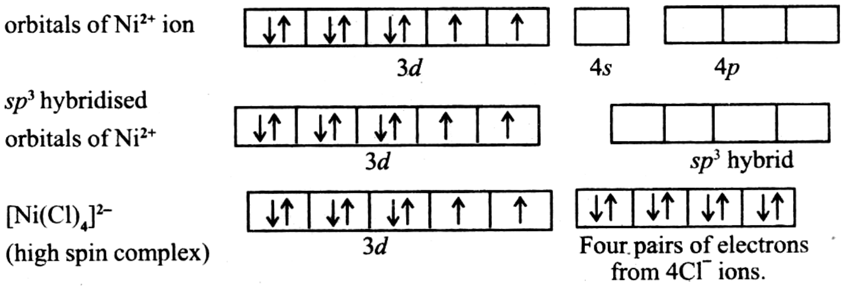


Formation of square planar $[Ni(CN)_4]^{2-}$ complex involving dsp^2 hybidisation of Ni^{2+} ion orbitals

The hybridisation involved here in dsp^2 and the structure is square planar. In this case one of the 3d orbitals is made empty and available for hybridisation. This is possible only by the fact that the two unpaired electrons are paired by the energy available due to the approach of the ligands. The four hybrid orbitals are occupied by four pairs of electrons, one from each CN^- ion. Since there are no unpaired electrons the complex is considered to be diamagnetic in nature (n=0). The empty hybrid orbitals of the metal overlap with the completely filled orbitals of CN^- ions to form metal- ligand co-ordinate bonds.

(2) Tetrachloridonickelate (II) ion, $(Ni(Cl)_4]^{2-}$

The nickel (II) ion has two unpaired electrons as shown below in Fig. Since the complex is paramagnetic it would involve unpaired electrons and sp^3 hybridisation. The structure istetrahedral.



(Cl^- is a weaker ligand.)

Formation of tetrahedral $[NiCl_4]^{2-}$ complex involving SP^3 hybridisation of Ni^{2+} ion orbitals.

The four hybrid orbitals are occupied by four pairs of electrons, one from each Cl^- ion. Since there are unpaired electrons the complex is considered to be paramagnetic.

Magnetic Properties of Co-ordination Compounds

Magnetic susceptibility experiment measures the magnetic moment of coordination compounds. The results obtained reveal the structures adopted by the metal complexes. Let us take the cases of 1st row transition metal series. The magnetic data of co-ordination compounds of these metals reveal some complications. In case of metal ions Ti^{3+} (d^1), V^{3+}(d^2), Cr^{3+} (d^3), two vacant d-orbitals are available for d^2sp^3 hybridisation with 4s and 4p orbitals having octahedral geometry. The magnetic behaviour of coordination compounds of these ions are similar.

But when there are more than three 3d electrons, the vacant pair of d-orbitals is available only by pairing. So for d^4 (Cr^{2+}, Mn^{3+}), d^5(Mn^{2+}, Fe^{3+}) and d^6(Fe^{2+}, Co^{3+}), as a result of pairing of d-orbitals two, one and zero unpaired electrons are left respectively. Maximum complications arise with species having d^4 and d^5 ions, e.g. $[Mn(Cl_6)]^{3-}$ has a magnetic moment, of two unpaired electrons whereas $[MnC_6]^{3-}$ has a paramagnetic moment of four unpaired electrons. $[CoF_6]^{3-}$ is paramagnetic with four unpaired electrons whereas $[Co\ (C_2O_4)_3]^{3-}$ is diamagnetic. $[Fe(CN)_6]^{3-}$ has a magnetic moment of a single unpaired electron whereas $[FeF_6]^{3-}$ has a paramagnetic moment of five unpaired electrons.

This anomaly is, however, explained by Valence Bond Theory on the basis of inner orbital and outer orbital complex formation. The co-ordination complex ion like $[Mn(CN_6)]^{3+}$, $[Fe\ (CN)_6]^{3-}$ and $[Co\ (C_2O_4)_3]^{3-}$ are inner orbital complexes involving d^2sp^3 hybridisation. But the former two are paramagnetic whereas the latter one is diamagnetic. Similarly, the complexes like $[MnCl_6]^{3-}$, $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$ are outer orbital complexes involving sp^3d^2 hybridisation and are paramagnetic having 4,5 and 4 unpaired electrons respectively.

Limitations of Valence Bond Theory

(1) The colour exhibited by co-ordination compounds can not be explained by the theory.

(2) The quantitative interpretation of magnetic data can not be made by this theory.

(3) The thermodynamic and kinetic stability of co-ordination compounds can not be explained by the theory.

(4) The theory can not distinguish between weak and strong ligands.

(5) The theory fails to predict the number, position and intensities of the bonds observed in electronic spectra of coordination compounds.

(6) The theory does not explain satisfactorily why some complexes of a metal ion in a particular oxidation state are low spin (inner orbital) whereas some other complexes of the same metal ion in the same oxidation state are high spin (outer orbital) e.g. $[Co(NH_3)]^{3+}$ is diamagnetic and $[CoF_6]^{3-}$ is paramagnetic.

(7) Exact predictions regarding the structure of 4-coordinate complexes whether tetrahedral or square planar can not be made by this theory.

Lecture - 60

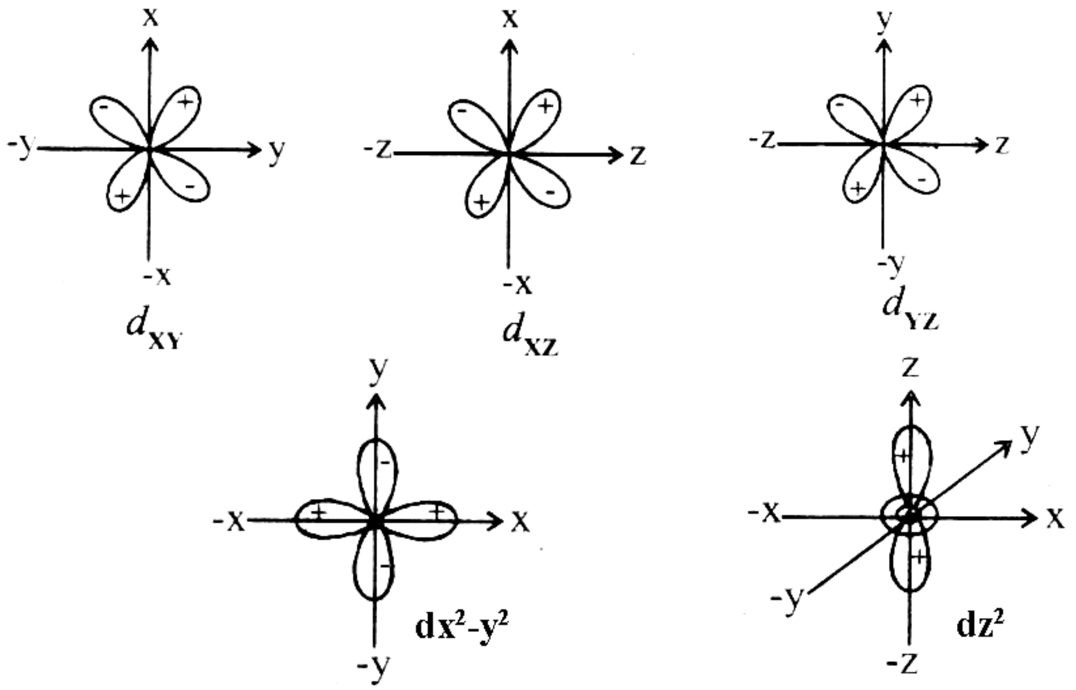
CRYSTAL FIELD THEORY

The theory was developed by H. Bethe and V. Bleck. According to this theory the bonding between a central metal ion and its ligand arises from purely electrostatic interactions. The ligand may be an anion or a neutral molecule having unshared or lone pair of electron. In case of anion the ligands are treated as point charges whereas in case of neutral molecules these are treated as dipoles. If the ligand is an anion the attraction between the central ion and the ligand is same as that between two oppositely charged particles. If the ligand is a dipole the negative end of the dipole is attracted towards the central positive ion.

The five d-orbitals is an isolated gaseous atom or ion are degenate i.e. they have the same energy. The degeneracy is maintained if the metal ion is surrounded by spherically symmetrical field of negative charges. But when the metal ion is surrounded by the ligands in a complex, the negative field becomes asymmetrical and the degeneracy of the d-orbital is destroyed or lifted. It results in splitting of d-orbitals. The nature of crystal field affects the pattern of splitting.

Orientation of d-orbitals and Crystal field splitting of Energy levels.

Depending upon the nature of orientation in space the d-orbitals are divided into two groups. Three orbitals belonging to one group are oriented in the regions in between the coordinate axes and are designated as d_{xy}, d_{yz}, d_{xz} while the other two orbitals belonging to another group or oriented along the axes and are designated as $d_{x^2-y^2}$ and d_{z^2}. In case metal ion, all the five d-orbitals are degenerate i.e. they are of equal energies.



Shape of d-orbitals

Now consider the case when the five rf-orbitals of the metal ion are surrounded by the negative charge of the ligands (anion or dipole). The energy of the orbitals lying along the axes i.e in the direction of point charges would be raised to a larger extent than that of the orbitals lying in between the axes. The splitting of five degenerate d-orbitals of the metal ion into set of orbitals having different energies is called **crystal field splitting.**

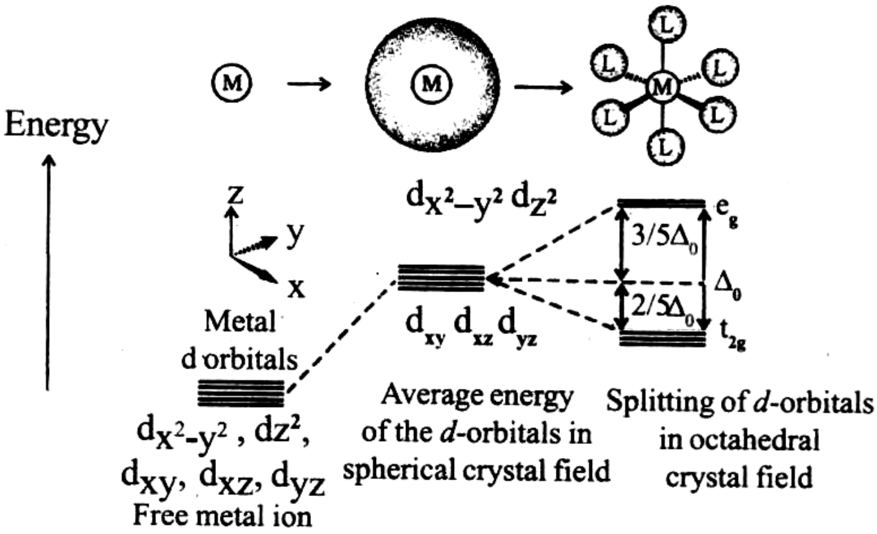
Crystal field splitting in Octahedral complexes

In an octahedral complex there are six ligands surrounding the metal atom or ion. Repulsion takes place between the electrons in metal d-orbitals and electrons of the ligands. The repulsion is more pronounced when the metal d-orbital is directed towards the ligand than when directed away from the ligand. As a result $d_{x^2-y^2}$ and d_{z^2} orbitals which point towards the axes along the direction of the ligand will experience more repulsion than d_{xy}, d_{yz} and d_{xz} orbitals which are directed between the axes. The energy of d_{xy}, d_{yz} and d_{xz} will be raised while that of d_{xy}, d_{yz} and d_{xz} will be lowered compared to the average energy in spherical Crystal Field. Thus due to metal electron - ligand electron repulsion the degeneracy of the d-orbitals has been lost in octahedral complex. Two sets of d-orbitals are formed.

(i) t_{2g} set comprising of three orbitals of lower energy, d_{xy} d_{yz} and d_{zx}

(ii) e_g set having two orbitals of higher energy, $d_{x^2-y^2}$, d_{z^2}

The energy separation between the two sets is represented by Δ_0 (The subscript 'o' is for octahedral) The energy of two e_g orbitals increases by (3/5) Δ_0 or $0.6\Delta_0$ or 6Dq and that of three t_{2g} decreases by (2/5) Δ_0 or 0.4 Δ_0 or 4Dq



d-orbital splitting in an octahedral crystal field

The factors that affect the crystal field splitting are (i) charge on the meal ion (ii) field produced by the ligand. The splitting will be large if the ligands produce strong field whereas the splitting will be small if the ligands produce weak field. The ligands may be arranged in the increasing order of the field strength produced by them in a series known as **spectrochemical series** as shown below.

$$I^- < Br^- < SCN^-Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$$

The series is based on absorption of light by complexes with different ligands.

Crystal Field Stabilisation Energy (CFSE)

The electron always prefers to occupy orbital of lower energy. In an octahedral complex containing one d-electron, it is evident that the electron would occupy one of the t_{2g} orbitals. This orbital has energy -0.4 Δ_0 compared to energy zero for hypothetical degenerate d-orbitals. Thus the complex will be 0.4 Δ_0 more stable than predicted by electrostatic theory. The decrease in energy 0 - (-0.4 Δ_0 = 0.4 Δ_0 is known as the **crystal field stabilisation energy** of the complex under consideration.

For a d^2 system, the two d-electrons will prefer to occupy t orbitals. The CFSE is $2\times0.4\ \Delta_0 = 0.8\Delta_0$. For a d^2 system the CFSE similarly is $3\times0.4 = 1.2\,\Delta_0$

But for a d^4 system there are two possibilities.

Configuration-

(1) All the four may occupy the three 2g orbitals. So one electron must be paired.

(2) Three electrons occupy t_{2g} orbitals and one electron e_g orbital

– –   ↑ –

d^4 :   ↑↓ ↑ ↑   ↑ ↑ ↑

(1) strong field $(\Delta_0 >>)$ (2) weak field $(\Delta_0 >>)$

The actual configuration is decided by taking into account Δ_0 and P (Pairing energy i.e the energy required for pairing the electrons)

(a) If $\Delta_0 > P$, configuration (1) is possible. The complex has less number of unpaired electrons and it is known as low spin or strong field complex.

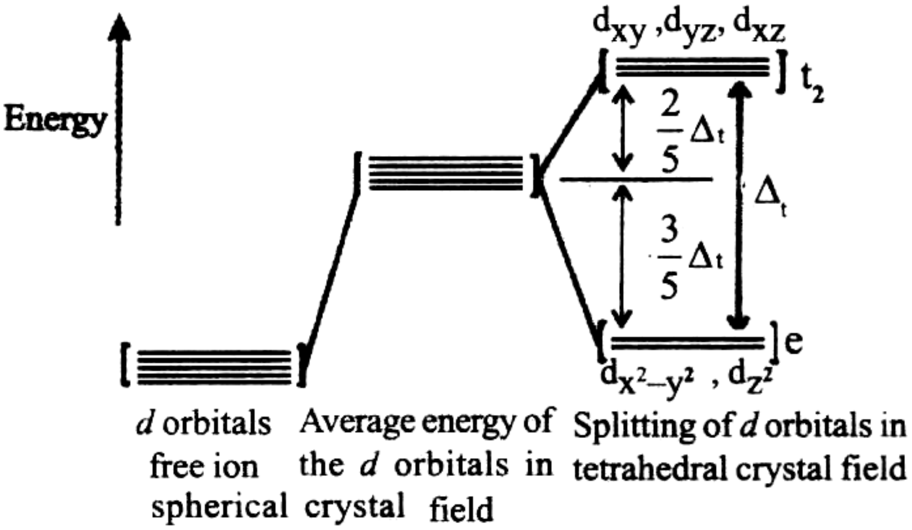
(b) If $\Delta_0 < P$, configuration (2) is possible. The complex has maximum number of unpaired electrons and it is known as high spin or weak field complex.

From detailed calculation it is found that d^4 to d^7 coordination complexes are more stable for strong field as compared to weak field cases.

Crystal Field splitting in Tetrahedral complexes

In a tetrahedral complex there are four ligands surrounding the metal atom or ion. The d-orbital splitting in this case is inverted and is smaller as compared to the octahedral splitting. Forthe same metal ion and same ligand and metal-ligand distance it is observed that $\Delta_t = 4/9\,\Delta_0$

Pairing of electrons in the orbital does not take place easily since orbital splitting energies are not sufficiently large for forcing pairing. So low spin configurations are almost not observed.



d- orbital splitting in an tetrahedral crystal field.

Colours in Coordination compounds.

A substance which possesses the property of absorbing certain radiations from the visible region (3800A^0 - 7600A^0) of the spectrum exhibits colour. So when white light in passed through the sample of co-ordination compound some of the visible spectrum is removed from the white light. The colour of the complex is complementary to that which is absorbed. The complementary colour is the colour produced from the wave length of visible light left over. For example if red light is absorbed by the complex it appears blue. Hydrated copper ions absorb red light and thus appear blue. (Munsell wheel)

Relationship between the Wavelength of Light absorbed and the Colour obsrved in some Coordination Entities

Coordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of Coordination Entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow	Violet
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green	Red
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow Orange
$[Co(CN)_6]^{3-}$	310	Ultraviolet	Pale Yellow
$[Cu(H_2O)_4]^{2+}$	600	Red	Blue
$[Ti(H_2O)_6]^{3+}$	498	Blue Green	Violet

In case of transition metal complexes the energy difference between two sets of d-orbitals is small. So the excitation of electron from t_{2g} orbital to e_g orbital involves absorption of low energy radiation and as a result the complex appears coloured. The complex $[Ti(H_2O)_6]^{3+}$ is having octahedral geometry. It has d^1 configuration. It absorbs radiations in the green and yellow regions corresponding to wave length around $5000A^0$. This corresponds to energy 240 kJ ($\because$ $E = h\nu = \frac{hc}{\lambda}, h =$ Planck's constant, c = velocity of light) This energy (equals to Δ_0) is required to cause promotion of electron from t_{2g} to e_g orbital. The solution of the complex looks purple which is the complementary colour to the absorbed colour.

Since the value of Δ_0 depends upon the nature of ligands, nature of ions and geometry of the complex formed, different coordination compounds absorb radiations from different regions of visible light and exhibit different colours, e.g. octahedral $[Co(H_2O)_6]^{2+}$ absorbs in blue region and appears pink (red). Tetrahedral $[CoX_4]^{2-}$ absorb in red region and appears blue. $[Co(NH_3)]^{3+}$ absorbs in blue region and appears orange in solution.

Transition metal ions having completely filled orbitals or completely empty orbitals are colourless. So complexes of $Cu^{+}(d^{10}), Zn^{2+}(d^{10}),$ $Ag^{+}(d^{10}),$ $Sc^{3+}(d^{0}), Ti^{4+}(d^{0})$ etc. are colourless.

Limitations of CFT (Crystal Field Theory) -

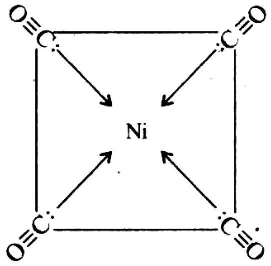
(1) Anionic ligands are found at the low end of spectrochemical series inspite of the fact that they produce greatest splitting effect.

(2) It is not concerned with the covalent character of metal-ligand bond.

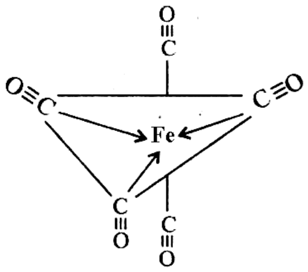
BONDING IN METAL CARBONYLS :

In metal carbonyls, a metal atom is directly linked to the carbon atom of a carbonyl group. Metal carbonyls possess simple structures, in which electrons forming $OC \rightarrow M$ bond are furnished by CO molecules. For this, metal atom in carbonyls is said to be in zero oxidation state. Basing on the number of metal atoms present, these may be (i) mononuclear carbonyls, M(CO) and (ii) polynuclear carbonyls. $M_x(CO)_y$.

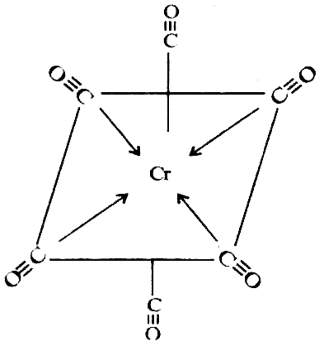
According to Valence Bond Theory, the structures of the carbonyls are explained on the basis of nature of hybridisation of atomic orbitals. For example, $Ni(CO)_4$ is tetrahedral, $Fe(CO)_5$ is trigonal bipyramidal and $Cr(CO)_6$ is octahedral.



(a) $Ni(CO)_4$



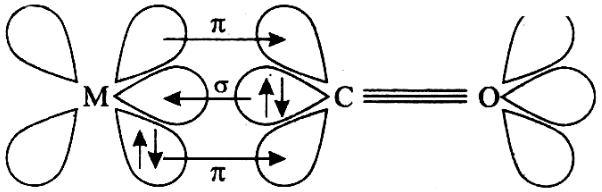
(b) $Fe(CO)_5$



(c) $Cr(CO)_6$

From the X-ray or electron diffraction method, it is found that the metal-carbon bonds are intermediate between the $M - C \equiv 0$ and $M = C \equiv O$ states, i.e. there is some double bond character in M - CO. Thus, it can be said that a M - C σ bond is formed along with M - C π bond. While the M - C σ - bond involves the donation of lone pair of electrons on the carbonyl carbon atom to an empty metal orbital, the M - C π bond is formed by dative overlapping of a filled d-orbital of metal with empty antibonding p-orbital of the carbon atom.

$$\text{Metal} \underset{\text{dative } \sigma \text{bond}}{\overset{\text{dative } \pi \text{ bond}}{\rightleftarrows}} \text{carbon monoxide}$$



M → C π bond and M ← C σ bond

(Synergic bonding)

STABILITY OF CO-ORDINATION COMPOUNDS :

While studying the stability of a coordination compound formed in solution, following stepwise addition ofligands to a metal ion is considered. Formation of the complex, ML_n is supposed to take place by the following n consecutive steps.

$$M + L \rightleftharpoons ML \qquad : K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \rightleftharpoons ML_2 \qquad : K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \rightleftharpoons ML_3 \quad : K_3 = \frac{[ML_3]}{[ML_2][L]}$$

$$ML_{n-1} + L \rightleftharpoons ML_n \quad : K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

Where K_1, K_2, K_3, ... K_n are referred to as stepwise stability constants and the overall stability constant K is expressed as :

$$M + nL \rightleftharpoons ML_n \qquad K = K_1K_2K_3.......K_n = \frac{ML_n}{[M][L]^n}$$

Greater the value of the overall stability constant, more will be the stability of the complex. The reciprocal of stability constant is called dissociation constant or instability constant (1/K).

The value of stability constant depends on the nature of the metal ion and the ligand. It is observed that, higher the charge density on the central metal ion more is the stability of its complexes, i.e. for a bigger value of $\frac{\text{charge}}{\text{radius of ion}}$, stability of its complex has a bigger value too. Again, more basic nature of a ligand also accounts for greater stability of the complex, as the donation of lone pairs of electrons by the ligands becomes easier.

IMPORTANCE OF COORDINATION COMPOUNDS.

1. In Qualitative analysis

The coordination compounds are of great importance and have wide range of applications. Since they are present in the mineral, plant and animal world they find extensive use in analytical chemistry, metallurgy and biological systems.

In qualitative analysis the detection and estimation of metal ions by chemical and instrumental methods of analysis are based on colour reactions with a number of chelating ligands resulting in the formation of coordination entities. Examples of such chelating ligands include EDTA (estimation of Ca^{2+}/Mg^{2+}), DMG (qualitative & quantitative determination of Ni^{2+}) etc.

2. Extraction of metals

Extraction processes of metals like silver and gold make use of complex formation. In presence of oxygen and water gold combines with cyanide to form the complex ion $[Au(CN)_2]^-$ in aqueous solution. By adding zinc to this solution, gold can be separated in the form of metal. Purification of metal can also be made through complex formation. For example, impure nickel is converted to $[Ni(CO)_4]$ which on decomposition yields pure nickel.

3. In Biological systems

We know that chlorophyll is very much necessary for the process of photosynthesis. It is a coordination compound of magnesium, The coordination compound of iron is haemoglobin which acts as an oxygen carrier. Vitamin B_{12} known as cyanocobalamine is an antipernicious anaemia factor. It is a coordination compound of cobalt. Similarly many enzymes coordinate with metal ions forming coordination compounds which are of great importance in biological systems.

ORGANOMETALLIC COMPOUNDS :

Introduction :

Compounds containing atleast one carbon-metal bond are called organometallic **compounds.** The first organometallic compound was prepared by Zessie in 1830 by the action of ethylene on a solution of potassium chloroplatinate (II). Quite a good number of such compounds have been synthesised and investigated during the last few years. Grignard reagent, R Mg X is a familiar example of organometallic compounds where R is an alkyl group. Other organometallic compounds include diethyl zinc $[Zn(C_2H_5)_2]$, teraethyl lead $[Pb (C_2H_5]_4$ dibenzene chromium $[Cr(C_6H_6)_2]$, ferrocene $[Fe(C_5H_5)_2]$ and metal carbonyls.

Classification (Three classes) :

1. Sigma (σ) bonded complexes. RMgX, $(C_2H_5)_2Zn$
2. Pi (π) bonded complexes.Zeise's salt, dibenzene chromium
3. Complexes containing both σ -and π -bonding characteristics. metal carbonyls

HOME ASSIGNMENT

1. Write down the fomula of the following complex :
   - (i) Potassium trixalatoforrate (III)
   - (ii) Potassium ammine trichlorido platinate (II)
   - (iii) Lithium tetra hydridoaluminate (III)
   - (iv) Hexaammine cobalt (III) chloride
   - (v) Sodium tetracyanido cuprate (II)
2. Provide one example in each case of outerorbital and inner orbital complex.
3. Show that $[Fe(CN)_6]^{4-}$ is diamagnetic while $\left[Fe(CN)_6\right]^{3-}$ is paramagnetic.
4. Predict the number of unpair $\overline{e}(s)$ in the following :

   $$\left[Cr(NH_3)_6\right]^{3+}, \left[Zn(NH_3)_4\right]^{2+}, \left[Ni(CO)_4\right][CoF_6]^{3-}, \left[Cu(NH_3)_4\right]^{2+}$$

5. Caclulate the μ_{eff} of $\left[Co(CN)_6\right]^{3-}$ and $\left[Co(H_2O)_6\right]^{3+}$

LECTURE - 62 AND 63

UNIT- X

ORGANIC CHEMISTRY

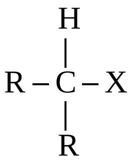
Haloalkanes - The halogen derivaties of alkanes, are called haloalkanes.

When only one hydrogen atom of an alkane is replaced by a halogen atom (X) (X = F, Cl, Br, I), the compound obtained is called monohalogen derivative of alkane. Its general formula is $C_nH_{2n+1}X$ or RX. Monohaloalkanes are of three types :

(i) Primary monohaloalkane - Their general formula is RCH_2X where 'R' may be 'H' or any alkylgroup.

Example - CH_3Br, CH_3CH_2Br etc.

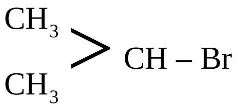
(ii) Secondary monohaloalkane - General formula is



$$R-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-X$$

or R_2CHX.

Example :

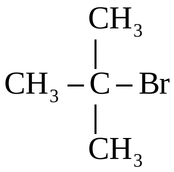


$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} > CH - Br$$

(2-bromopropane)

(iii) Tertiary monohaloaleave - General formula is $R_3C - X$.

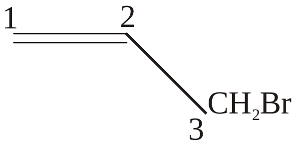
Example



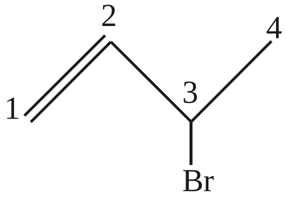
$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Br$$

(2-brmo-2-methyl propane)

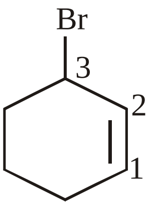
Allylic halides :- in these halides, the halogen atom is linked to a sp^3-hybridised carbon atom which is next to a carbon-carbon double bond is to an allylic carbon. These may further be classified as 1^0, 2^0 or 3^0.



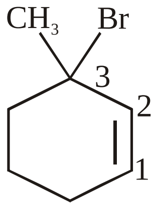
3-bromopropene (1^0)
(Allylhalide)



3-bromo but-1-ene (2^0)
An allylic halide



3-bromo cyclohex-l-ene (2^0)
(An allylic halide)



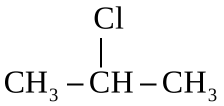
3-bromo-3-methyl cyclohexe-1-ene(3^0)
(An allylic halide)

Nomenclature of haloalkanes - The common names of alkylhalides are derived by naming the alkyl group followed by the halide (X fluoride, chloride, bormide or iodide). In IUPAC system they are named as halosubstituted hydrocarbons. Halo areas are the common as well as IUPAC names of axyl halides.

$CH_3CH_2CH_2Br$

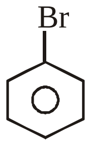
n-propyl bromine (common name)

1-Bro propane (IUPAC)

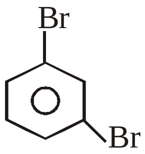


$CH_3-\overset{Cl}{\overset{|}{C}}H-CH_3$

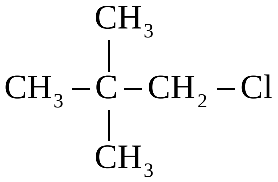
(isopropyl chloride) 2-chloro propane



Bromobenzene



1,3-dibromobenzene



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-Cl$

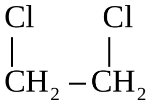
1 – chloro – 2, 2 – dim ethyl propane.

Dihaloalkanes having same type of halogens are named as alkylidene or alxylene dihalides. In common name system, gem-dihalides are named as alkylidene-halides and vic-dihalides are named as alkylene dihalides. In IUPAC system they are named as dihaloalkanes.

CH_3CHCl_2

(Ethylidene chloride

(Gen – dihalide)



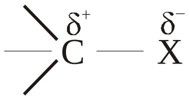
$\overset{Cl}{\overset{|}{C}}H_2-\overset{Cl}{\overset{|}{C}}H_2$

Ethylene dichloride (vic-dihalide)

IUPAC name – 1,1-Dichloroethane

1,2-Dichloro ethane.

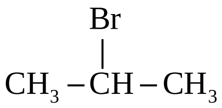
Nature of C-X bond : Because of higher electronegativity of halogen atom than carbon atom, the halogen atom bears a partial negative charge.



Due to increase in size of halogen atom from F to I, the carbon-halogen bond length increases from C-F to C-I.

Isomerism - Haloalkanes exhibit position isomerism, in which the halogen atom occupies different position in the chain.

Example- $CH_3–CH_2–CH_2–Br$ (1-Bromopropane)

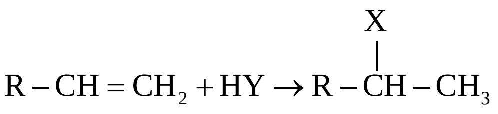


$CH_3-\overset{Br}{\overset{|}{C}}H-CH_3$ (2-Bromo propane)

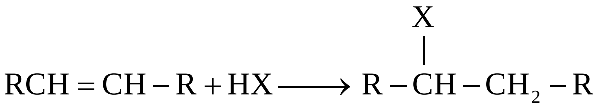
Preparation of Haloalkanes - Haloalkanes can be prepared from alkanes, alkenes, alcohols & mono-carboxylic acids.

(1) From alkanes $RH+X_2\xrightarrow{hv}RX+HX\ (x=Cl\ or\ Br)$

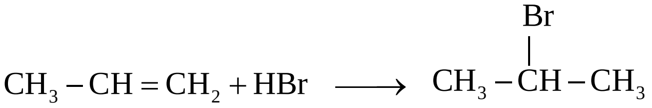
Example $CH_4+Cl_2\rightarrow CH_3Cl+\xrightarrow{Cl_2}CH_2Cl_2\xrightarrow{+Cl_2}CHCl_3\xrightarrow{Cl_2}CCl_4$



From alkenes $R-CH=CH_2+HY \rightarrow R-\overset{\overset{X}{|}}{C}H-CH_3$ (Addition follows Markiwnikoff's rule)



$$RCH=CH-R+HX \longrightarrow R-\overset{\overset{X}{|}}{C}H-CH_2-R$$



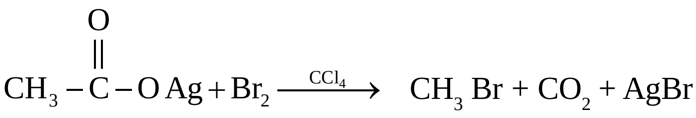
$$CH_3-CH=CH_2+HBr \longrightarrow CH_3-\overset{\overset{Br}{|}}{C}H-CH_3$$

$$CH_3-CH=CH_2+HBr \xrightarrow[\text{Anti markownikoff 's rule}]{\text{Organic peroxide}} CH_3–CH_2–CH_2Br$$

3. From Alcohol

$$ROH \begin{cases} \xrightarrow{+HX,\,anhZnCl_2} & RX+H_2O \\ \xrightarrow{Red\,P+Br_2(PB_3)} & RBr+H_3PO_3 \\ \xrightarrow{PCl_5} & R-Cl+POCl_3+HCl \\ \xrightarrow{SOCl_2} & R-Cl+SO_2+HCl \end{cases}$$

4. From monocarboxylic acid (Hunsidiecker Reaction) when silver salt of mono carboxylic acid is treated with Cl_2 or Br_2 in carbon tetrachloride solution, alkyl halides are formed



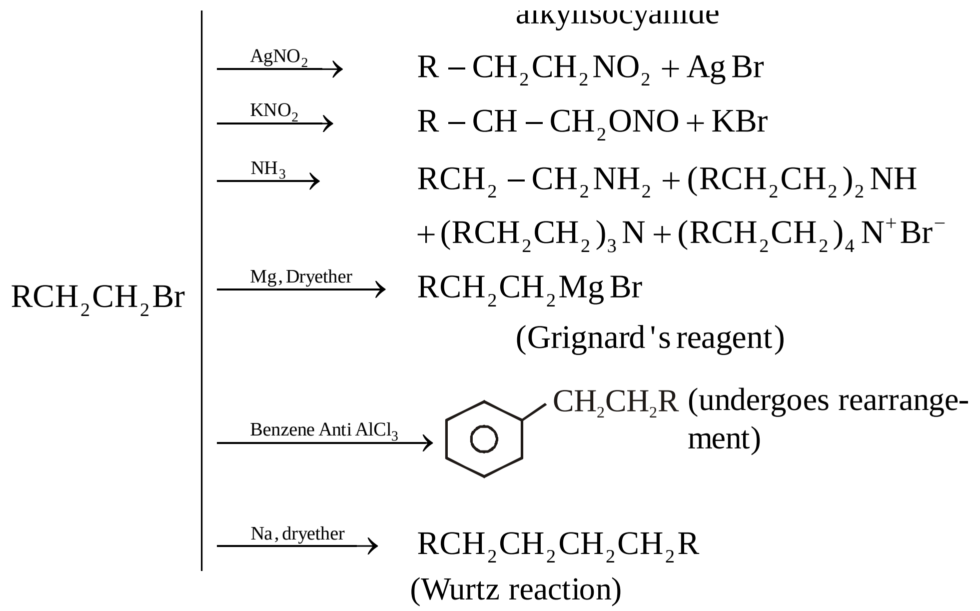
$$CH_3-\overset{\overset{O}{\|}}{C}-O\,Ag+Br_2 \xrightarrow{CCl_4} CH_3\,Br+CO_2+AgBr$$

Properties :

1. Lower alkyl halides like CH_3Cl, CH_3Br, C_2H_5Cl are gases but CH_3I and rest of lower member halides upto C-atom 18 are colourless liquids.
2. Alkyl halides are slightly polar. They are insoluble in water but more soluble in organic solvents like benzene, ether, alcohols etc.
3. Alkyl halides have boiling point higher than the corresponding hydrocarbons.
   B.P. of RI > RBr > RCl

Chemical Properties

$$RCH_2CH_2Br \begin{cases} \xrightarrow{aq\,KOH} & RCH_2CH_2OH+KBr+H_2O \\ & \text{(alcohol)} \\ \xrightarrow{alc.\,KOH} & R-CH=CH_2+KBr+H_2O \\ & \text{(alkene)} \\ \xrightarrow{R'ONa} & R-CH_2-CH_2R'\text{(Ether)} \\ \xrightarrow{alcohol\,KCN} & RCH_2CH_2CN \\ \xrightarrow{AgCN} & (R-CH_2-CH_2-NC) \\ & \text{alkylisocyanide} \end{cases}$$



alkylisocyanide

$$RCH_2CH_2Br \xrightarrow{AgNO_2} R-CH_2CH_2NO_2 + AgBr$$

$$\xrightarrow{KNO_2} R-CH-CH_2ONO + KBr$$

$$\xrightarrow{NH_3} RCH_2-CH_2NH_2 + (RCH_2CH_2)_2NH + (RCH_2CH_2)_3N + (RCH_2CH_2)_4N^+Br^-$$

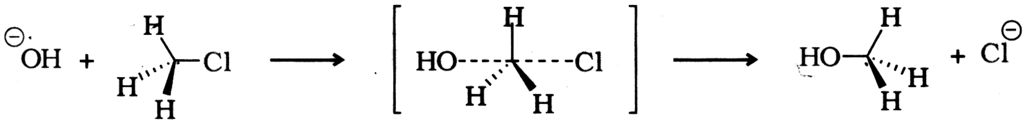
$$\xrightarrow{Mg,\ Dryether} RCH_2CH_2MgBr$$

(Grignard's reagent)

$$\xrightarrow{Na,\ dryether} RCH_2CH_2CH_2CH_2R$$

(Wurtz reaction)

Rate of reaction α [alkylhalide]. [nucleophile]



When the incoming nucleophile OH^- ion approaches the alkyl halides (CH_3Cl) molecule and starts interacting with it, the carbon-halogen bond starts breaking and new carbon –OH bond starts forming. These two processes take place simultaneously in a single step and reaction occurs through a transition state. It can be seen that in S_N2 reactions, the attack of the nucleophile (i.e. OH^- ion) leaves from the front side. As a result S_N2 reactions are always accompanied by inversion of configuration. This inversion of configuration is called Walden inversion.

The order of reactivity of alkylhalides towards S_N2 reactions are

1^0 alkylhalide > 2^0 alkylhalide > 3^0 alkyhalide

(ii) Substitution Nucleophilic Unimolecular (S_N2)

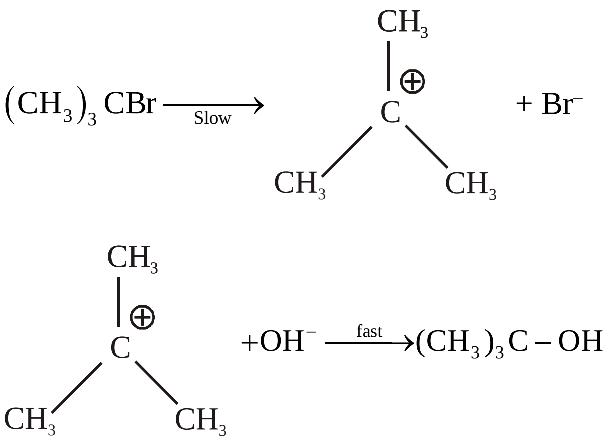
S_N1 reactions are usually carried out in polar protic solvents (like water, alcohol, acetic acid etc). The reaction between t-butyl bromide and hydroxide ion yields tert-butyl alcohol and follows first order kinetics is the rate of reaction depends upon the concentration of only one reactant which is tert-butyl bormide (substrate).

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3C-OH + Br^-$$

The reaction occurs in two steps :

In step I, the polarised C-Br bond undergoes slow cleavage to produce carbocation and a bromide ion.

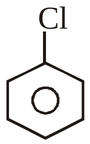
In step II, the carbocation thus formed is attacked by the nucleophile OH^- ion and the product is formed. This step is fast and hence does not affect the rate of reaction.



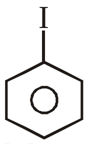
Lecture - 65

Haloarenes :- Haloarenes are compound formed by replacement of one or more hydrogen atoms of aromatic hydrocarbon by an equal number of halogen atoms.

Example : (1) Halogen atom attached tobenzene ring

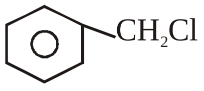


Chlorobenzene

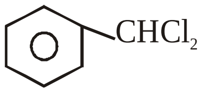


Iodobenzene

(2) Halogen atom attached to side chain

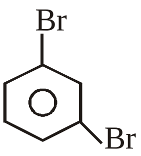


Benzyl Chloride

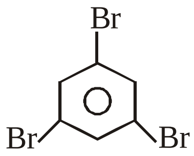


Benzaldichloride

Nomenclasture



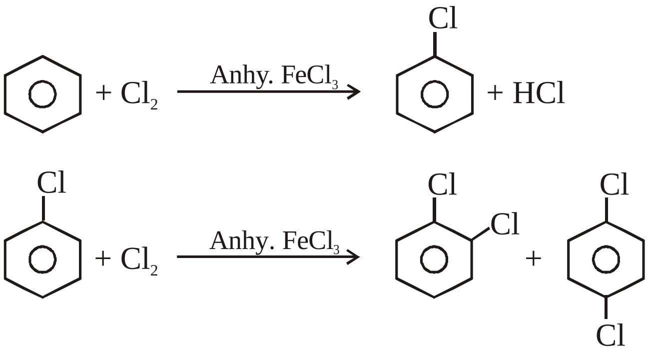
M-dibromo benzene
(1,3-dibromo benzene)

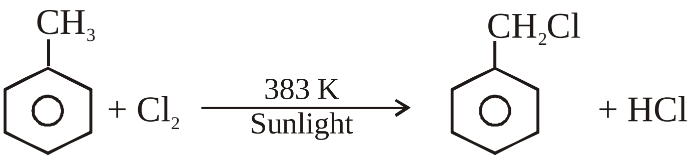


(1,3,5-Tribromo benzene)

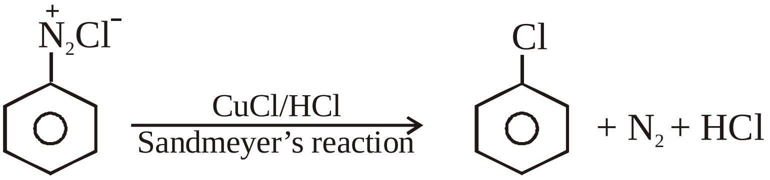
Preportion :

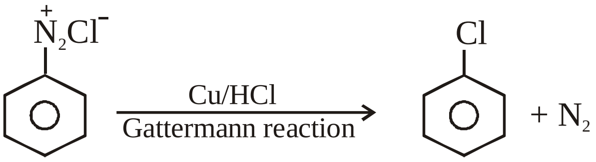
(1) From benzene

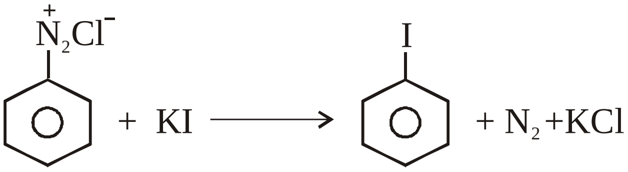


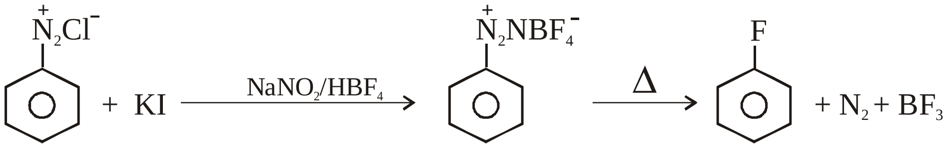


(2) From Benzene diazonium chloride



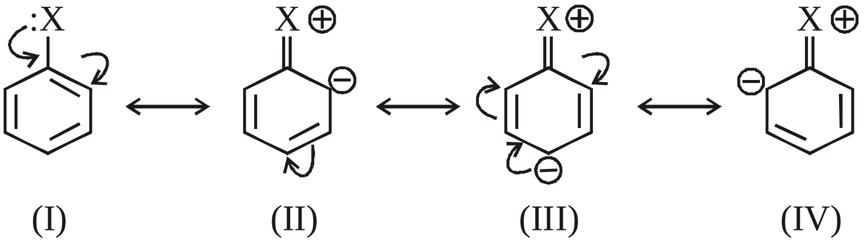




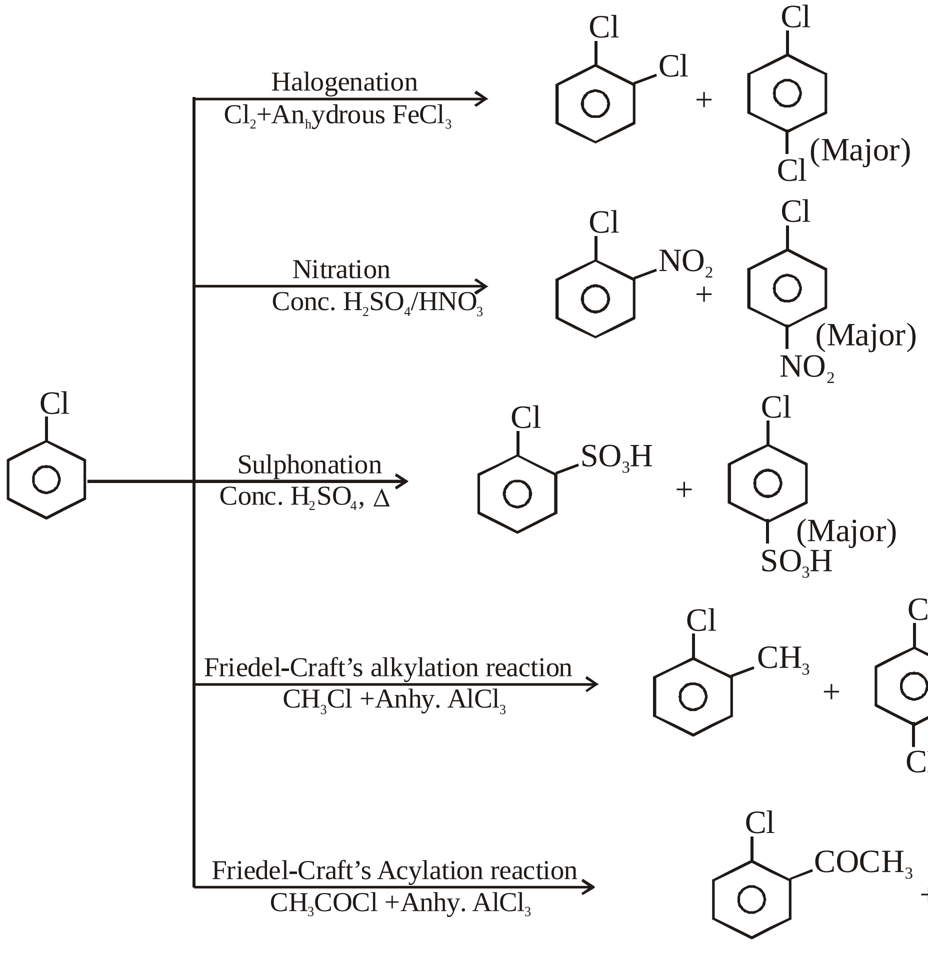


Propertion

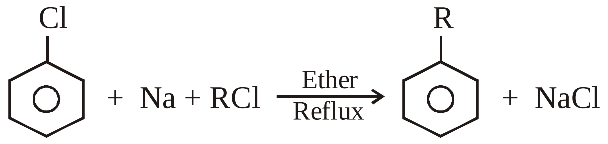
1. **Electrophilic Substitution Reactions :** Haloarenes undergo electrophilic substitution reactions like nitration, halogenation, sulphonation and Friedel-Craft's reaction. The halogen atom is ortho and p-directing that can be understood if we consider the resonating structures of halobenzene as shown.



Due to reesonance, the electron density increases more at ortho and para-positions than at meta-positions. Because of - I effect of halogen atom electrons are withdrawn from benzene ring. So the ring gets deactivated as compared to benzene and hence electrophilic substitution reactions in haloarenes occurs slowly.



2. Wurtz-Fitting Reaction - A mixture of alkyl halides and aryl halide when treated with sodium in dry ether give alkyl benzene.



Fitting Reactions :- Aryl halides when treated with sodium and dry ether to give diphenyl.

$$C_6H_5Cl + 2Na + C_6H_5Cl \xrightarrow{\text{Ether}} C_6H_5 - C_6H_5 + 2NaCl$$

3. **Ullmann biaryl synthesis** - When an iodobenzene is heated with copper power in a sealed tube, diaryl is formed.

$$C_6H_5I + 2Cu + IC_6H_5 \xrightarrow[\text{Sealed tube}]{\Delta} C_6H_5 - C_6H_5 + 2CuI$$

4. Reaction with magnesium :- Bromo and iodobenzenes form Grignard reagent when their ethereal solution is treated with magnesium.

$$C_6H_5Br + Mg \xrightarrow[\Delta]{\text{Dry ether}} C_6H_5MgBr.$$

5. Reaction with Lithium :- Bormo and iodobenzene react with lithium metal in dry ether medium to form phenyl lithium.

$$C_6H_5Br + 2Li \xrightarrow[\Delta]{\text{Dry ether}} C_6H_5Li + LiBr$$

Lecture - 66

Uses and Environmental effects of polyhalogen compounds

1. **Dichloro methane (CH_2Cl_2) -** It is used as solvent for paint remover, as a propellant in aerosols, and as a solvent for manufacture of drugs. It is also used as metal cleaning and finishing solvent.

Physiological effect -

(i) It harms human-central nervous system.

(ii) Exposure to small levels of methylene chloride chloride (CH_2Cl_2) in air can lead to slightly impaired hearing and vision.

(iii) Higher levels of methylene chloride in air causes dizziness, nausea and numbness of fingers and toes.

(iv) In humans direct skin contact with CH_2Cl_2 causes intense burning and mild redness of skin.

(v) Direct contact with the eyes can burn cornea.

2. Chloroform ($CHCl_3$) :

(i) It is used as solvent for fats, alkaloids and iodine.

(ii) The major use of chloroform today is the production the freon refrigerant R-22.

(iii) It is used as anaesthetics.

Physiological effects

(i) Inhaling chloroform vapours depresses the central nervous system.

(ii) Chronic chloroform exposure damages liver (where chloroform is metabolised to phosgene).

(iii) Breathing about 900 parts of chloroform permillion parts of air (900 ppm) for a short time causes dizziness, foatigue and headache.

3. Iodoform (Triodo methane) : Iodoform was earlier used as an antiseptic for dressing wounds. Its antiseptic properties are due to liberation of iodine and not due to iodoform itself.

4. Carbon tetrachloride (CCl_4)

(i) It is used for the manufacture of refrigerants and propellants for aerosol cans.

(ii) It is used as feedstock in the synthesis of chlorofluoro carbons (freons) and other chemicals.

(iii) Uses as solvent in the manufacture of pharmaceuticals.

Physiological effects :

(i) Exposure of CCl_4 causes liver cancer in humans.

(ii) The most common effects are diziness, light headaches, nausea & vomiting, which can cause permanent damage to nerve cells. These effects also lead to coma, or death.

(iii) When brought in contact with eyes, it causes irritation.

5. Freons : The chlorofluoro compounds of methane and ethane are collectively known as freons. From 12 (CCl_2F_2) is the most common freons in industrial use. These are produced for aerosol propellants, refrigeration and air-conditioning purposes.

Environmental effects :- Most freon even that used in refrigeration, eventually makes its way into the atmosphere where it diffuses unchanged into stratosphere. In stratospher, freon initiates radical chain reactions which can disrupt the natural ozone layer.

6. **DDT (P, P$^{/}$- Dichlorodiphenyl Trichloroethane)**

DDT is an insecticide. Its use was increased enormously after World War II, because of its effectiveness against the Anopheles mosquitoes which spread malaria and lice that carry typhus.

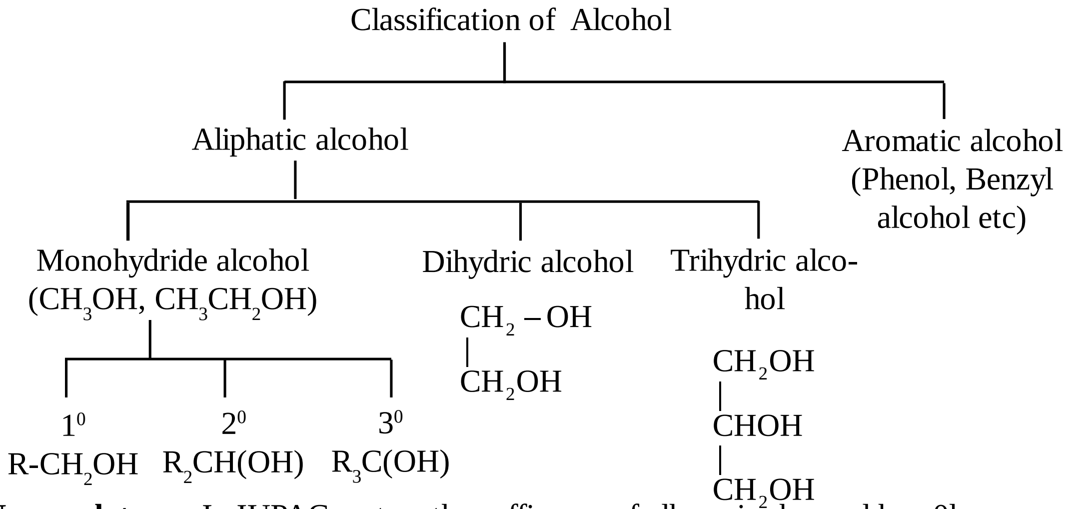
Tragic side effects :- Many species of insects developed resistance to DDT and it was discovered to have a high toxicity towards fish. DDT is not metabolised very rapidly by animals, so it is deposited and stored in fatty tissues. DDT affects reproductive system of animals.

7. **Benzene Hexachloride (BHC) ($C_6H_6Cl_6$)**

The insecticidal properties are due to one of the isomer i.e. $\nu-$isomer which is called Gammexane or Lindane. It is very stable and acts more quickly than DDT.

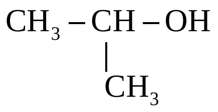
Lecture - 67 UNIT - XI

ALCOHOLS, PHENOS AND ETHERS



Nomenclature - In IUPAC system the suffix-ane of alkane is changed by –0l

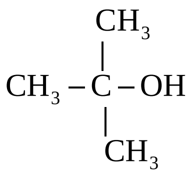
$CH_3OH \longrightarrow$ Methanol (1^0)



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH$

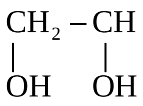
Propan-2-ol (2^0)

$CH_3CH_2–CH_2OH$ Propan-1-ol (1^0)



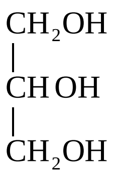
$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH$

2-Methyl propan-1-ol



$\underset{\displaystyle OH}{\underset{|}{CH_2}}-\underset{\displaystyle OH}{\underset{|}{CH}}$

Ethane – 1, 2 – diol



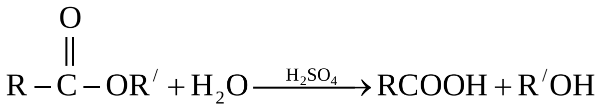
$\begin{array}{l} CH_2OH \\ | \\ CH\,OH \\ | \\ CH_2OH \end{array}$

Propane-1, 2, 3-triol

Methods of preparation of Alcohols

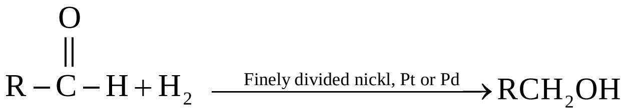
(1) By hydrolysis of Alkyl halide - $RX + aq.KOH \rightarrow ROH + KX$

(2) By hydrolysis of ester –

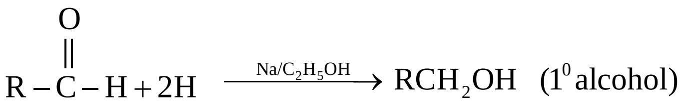


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + H_2O \xrightarrow{H_2SO_4} RCOOH + R'OH$$

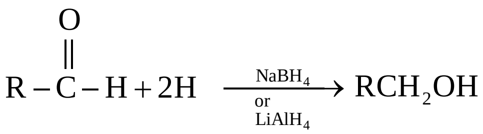
3. By reduction of aldehydes and ketones



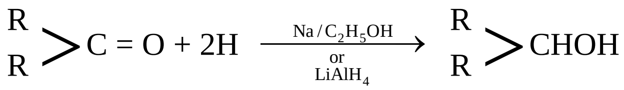
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2 \xrightarrow{\text{Finely divided nickl, Pt or Pd}} RCH_2OH$$



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H + 2H \xrightarrow{Na/C_2H_5OH} RCH_2OH \quad (1^0 \text{alcohol})$$



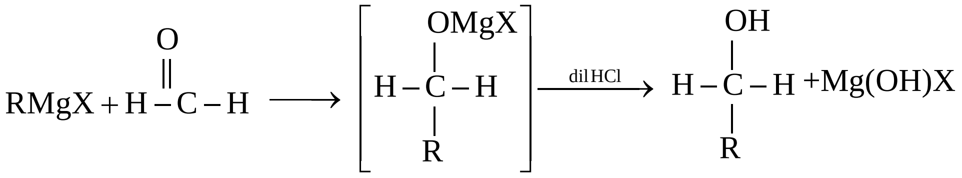
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H + 2H \xrightarrow[\text{or } LiAlH_4]{NaBH_4} RCH_2OH$$



$$\begin{matrix}R\\R\end{matrix}\!\!>C=O + 2H \xrightarrow[\text{or } LiAlH_4]{Na/C_2H_5OH} \begin{matrix}R\\R\end{matrix}\!\!>CHOH$$

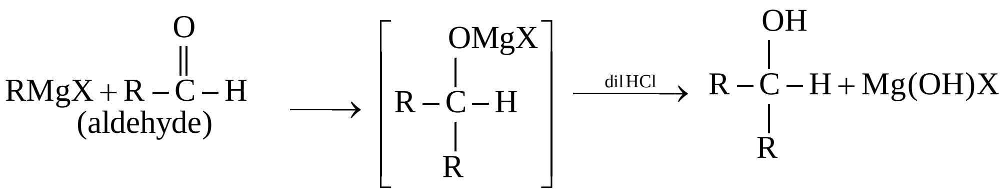
(2^0 alcohol)

4. From Grignard reagent by action with aldehydes or ketones.

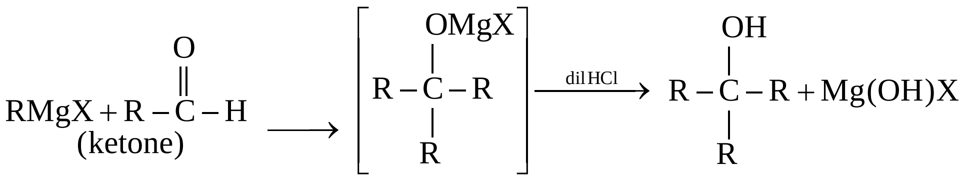


$$RMgX + H-\overset{\overset{\displaystyle O}{\|}}{C}-H \longrightarrow \left[H-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OMgX}{|}}{C}}-H\right] \xrightarrow{dil\,HCl} H-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-H + Mg(OH)X$$

(1^0 alcohol)



$$\underset{\text{(aldehyde)}}{RMgX + R-\overset{\overset{\displaystyle O}{\|}}{C}-H} \longrightarrow \left[R-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OMgX}{|}}{C}}-H\right] \xrightarrow{dil\,HCl} R-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-H + Mg(OH)X$$



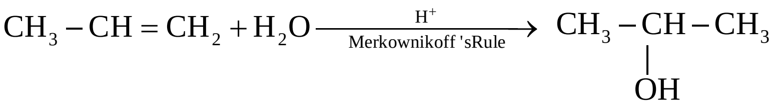
$$\underset{\text{(ketone)}}{RMgX + R-\overset{\overset{\displaystyle O}{\|}}{C}-H} \longrightarrow \left[R-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OMgX}{|}}{C}}-R\right] \xrightarrow{dil\,HCl} R-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-R + Mg(OH)X$$

5. From aliphatic primary amine.

$$R-NH_2 + HNO_2 \xrightarrow[O-5^0]{\text{Solid } NaNO_2 \text{ and dil HCl}} ROH + N_2 + H_2O$$

6. By acid catalysed hydration of alkenes

$$H_2C=CH_2 + H_2O \xrightarrow{H^+} CH_3-CH_2OH$$



$$CH_3-CH=CH_2+H_2O\xrightarrow[\text{Merkownikoff 'sRule}]{H^+}CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

7. **Hydroboration - Oxidation**

Alkenes undergo hydroboration with diborane to produce trialkyl boron (R_3B) which on subsequent oxidation with H_2O_2 in presence dil NaOH gives primary alcohol.

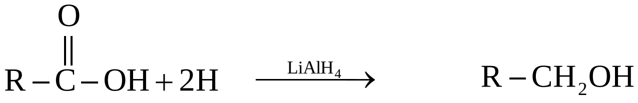
$$CH_2=CH_2+(BH_3)_2\rightarrow CH_3-CH_2-BH_2\xrightarrow{CH_2=CH_2}(CH_3CH_2)_2\,B.H$$

$$\xrightarrow{CH_2=CH_2}(CH_3CH_2)_3\,B\ \text{Triethyl boron.}$$

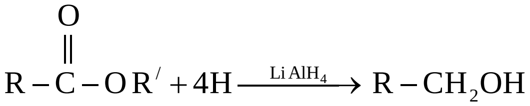
$$(CH_3CH_2)_3\,B+3H_2O_2\xrightarrow{OH^-}3CH_3CH_2OH+B(OH)_3\text{, Boric acid.}$$

N.B. Hydroboration - oxidation of propene produces propan-1-ol.

8. **By reduction of carboxylac acids and esters by Li Altter.**



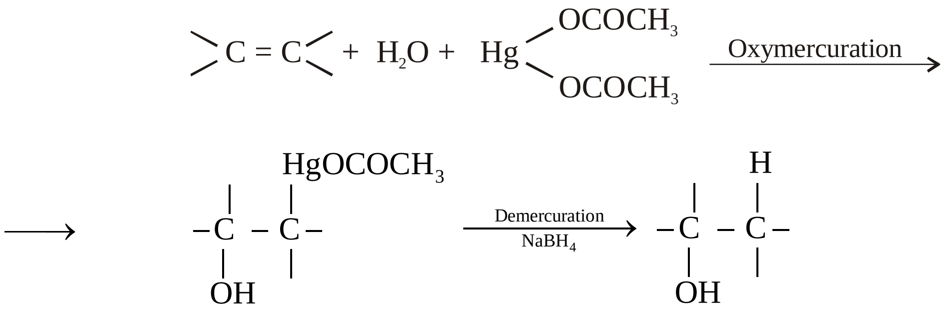
$$R-\overset{\displaystyle O}{\overset{\|}{C}}-OH+2H\xrightarrow{LiAlH_4}R-CH_2OH$$



$$R-\overset{\displaystyle O}{\overset{\|}{C}}-OR'+4H\xrightarrow{Li\,AlH_4}R-CH_2OH$$

9. **By oxymercuration - demercuration**

Alkenes react with mercuric acetate in presence of water to form hydroxy mercurial compounds which on subsequent reduction gives alcohols.



$$>C=C<+H_2O+Hg(OCOCH_3)_2\xrightarrow{\text{Oxymercuration}}-\underset{\displaystyle OH}{\underset{|}{\overset{|}{C}}}-\underset{|}{\overset{\displaystyle HgOCOCH_3}{\overset{|}{C}}}-\xrightarrow[NaBH_4]{\text{Demercuration}}-\underset{\displaystyle OH}{\underset{|}{\overset{|}{C}}}-\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}-$$

Physical Properties :

(i) At ordinary temperature, lower member of alcohols are colourless volatile liquids.

(ii) First three members are completely soluble in water & the solubility decreases with increase in molecular mass. The solubility in water is due to hydrogen bonding. With increase in molecular mass of alcohols, the non-polar part ofr hydrocarbon prevents H-bonding with water molecules, for which solubility decreases.

3. **Boiling point -** Boilinjg point of alcohols are much higher than the corresponding hydrocarbons of comparable molecular masses because of inter molecular hydrogen bonding. Branched chain alcohols have less surface area for which the boiling point decreases.

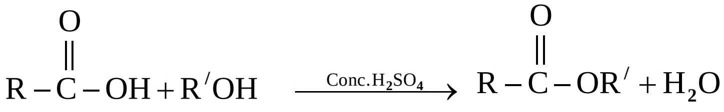
Lecture - 68

Chemical properties of primary alcohols

1. Reactions involving the cleavage of oxygen-hydrogen bond.

(a) Reaction with alkalimetal to form alkoxides. $ROH + Na \rightarrow RONa + 1/2H_2$.

(b) Reaction with carboxylic acids to form esters.



$$R-\overset{\overset{O}{||}}{C}-OH + R'OH \xrightarrow{Conc.H_2SO_4} R-\overset{\overset{O}{||}}{C}-OR' + H_2O$$

(c) Reaction with conc. HCl in presence of anhydrous $ZnCl_2$.

$$ROH + HCl \xrightarrow{\text{Anhydrous } ZnCl_2} RCl + H_2O$$

(d) Reaction with conc. H_2SO_4 at 140^0C form ether, but at 170^0C an alkene is formed.

$$C_2H_5OH + conc.H_2SO_4 \rightarrow C_2H_5HSO_4 + H_2O$$

$$C_2H_5HSO_4 + C_2H_5OH \xrightarrow{140^0\,C} C_2H_5OC_2H_5 + H_2SO_4$$

$$C_2H_5HSO_4 \xrightarrow{170^0\,C} CH_2 = CH_2$$

2. Reactions involving the cleavage of carbon-oxygen bond

(i) By reaction with PCl_5 and $SOCl_2$ an alkylhalide is formed.

$$ROH + PCl_5 \rightarrow RCl + POCl_3 + HCl$$

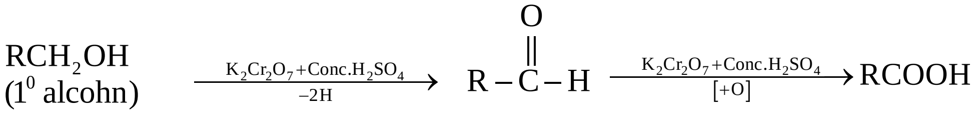
$$ROH + SOCl_2 \rightarrow RCl + SO_2 + HCl$$

Alcohols react with Red P & Br_2 (PBr_3) to form alkyl bromide

$$3ROH + PBr_3 \xrightarrow{\text{Red P} + Br_2} 3RBr + H_3PO_3$$

3. Reactions involving both alkyl & hydroxyl group

(a) Oxidation by acidified $K_2Cr_2O_7$ solution.

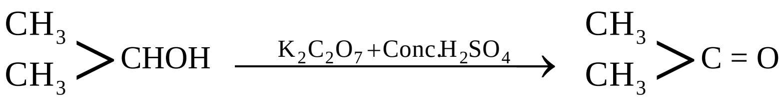


$$\underset{(1^0 \text{ alcohn})}{RCH_2OH} \xrightarrow[-2H]{K_2Cr_2O_7 + Conc.H_2SO_4} R-\overset{\overset{O}{||}}{C}-H \xrightarrow[{[+O]}]{K_2Cr_2O_7 + Conc.H_2SO_4} RCOOH$$

Oxidation by Pyridinium Chlorochromate (PCC) gives aldehyde. (PCC is the complex of CrO_3 with pyridine and HCl).

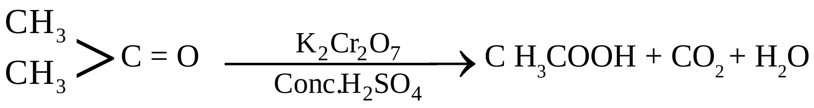
$$CH_3CH_2OH \xrightarrow{PCC} CH_3CHO.$$

(ii) Oxidation of 2^0 alcohol gives ketone



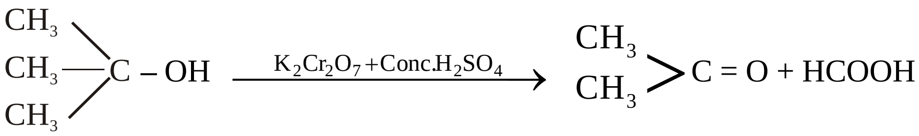
$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHOH \xrightarrow{K_2C_2O_7+Conc.H_2SO_4} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O$$

under drastic condition ketone is oxidised to carboxylicacids containing less no. of carbon atoms than original alcohol.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O \xrightarrow[Conc.H_2SO_4]{K_2Cr_2O_7} C\,H_3COOH + CO_2 + H_2O$$

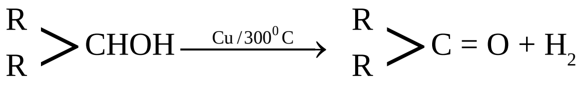
(iii) 3^0 alcohol on oxidation by $K_2Cr_2O_7$ & conc. H_2SO_4 at high temperature gives a mixture of ketone and a lower carboxylic acid.



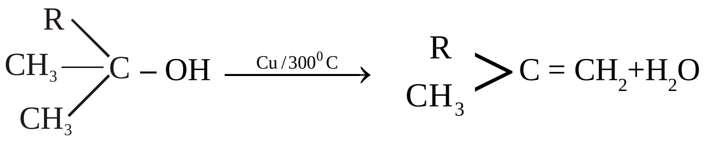
$$(CH_3)_3C-OH \xrightarrow{K_2Cr_2O_7+Conc.H_2SO_4} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O + HCOOH$$

(b) Catalytic dehydrogenation

$$RCH_2OH \xrightarrow{Cu/300^0C} RCHO + H_2$$



$$\begin{matrix}R\\R\end{matrix}\!\!>CHOH \xrightarrow{Cu/300^0C} \begin{matrix}R\\R\end{matrix}\!\!>C=O + H_2$$



$$R(CH_3)_2C-OH \xrightarrow{Cu/300^0C} \begin{matrix}R\\CH_3\end{matrix}\!\!>C=CH_2 + H_2O$$

(Here dehydration takes plate)

Lecture - 69

Identification of 1^0, 2^0 and 3^0 alcohols (Laboratory tests)

1. By Luca's reagent - (Equimolar mixture of Conc HCl and anhydrous $ZnCl_2$).

1^0, 2^0 and 3^0 alcohols are differentiated on the basis of the time required for appearance of alkyl halide turbidits.

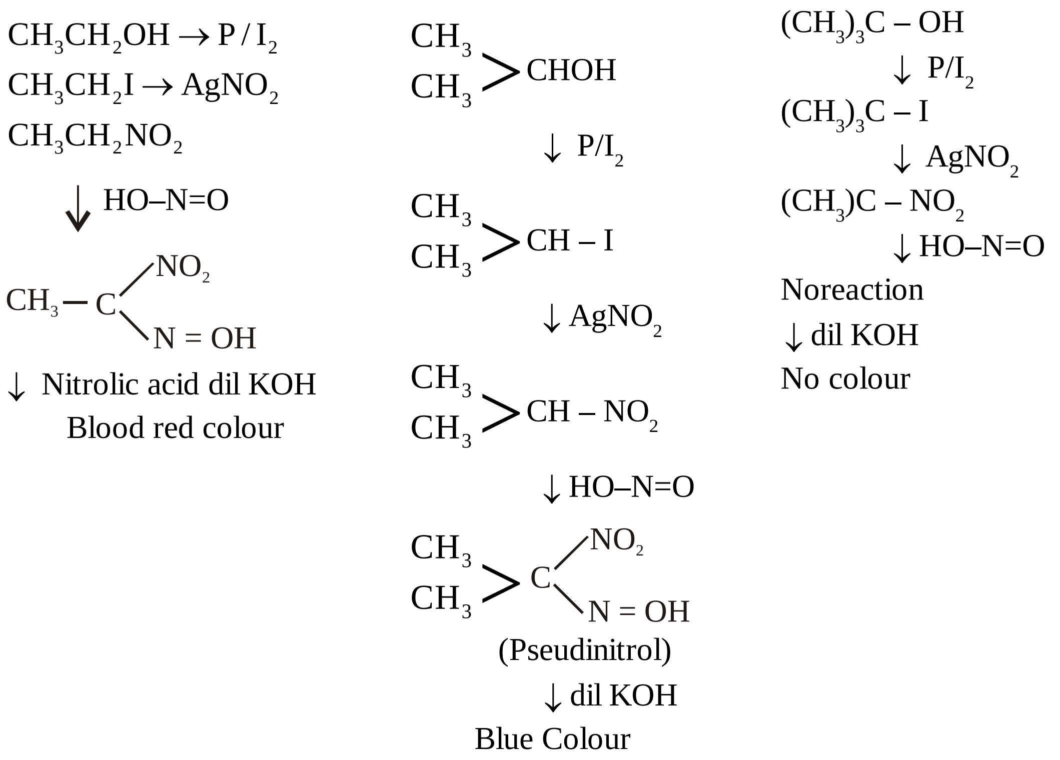
$$\underset{(3^0\,Alcohol)}{R_3C-OH} \xrightarrow{Conc.HCl+Anh-ZnCl_2} \text{Turbidity appears immediately}$$

$$\underset{(2^0\,alcohol)}{R_2CH-OH} \xrightarrow{Conc.HCl+Anh.ZnCl_2} \text{Trubidity appears after five minutes.}$$

$$R-CH_2OH \xrightarrow{Conc.HCl+Anh.ZnCl_2} \text{No trubicity appears even after several hours.}$$

2. Victor Meyer's Test

1^0 alcohol **2^0 alcohol** **3^0 alcohol**



1^0 alcohol:

$CH_3CH_2OH \rightarrow P/I_2$

$CH_3CH_2I \rightarrow AgNO_2$

$CH_3CH_2NO_2$

$\downarrow$ HO–N=O

$$CH_3-C\begin{matrix}\nearrow NO_2\\ \searrow N=OH\end{matrix}$$

$\downarrow$ Nitrolic acid dil KOH

Blood red colour

2^0 alcohol:

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHOH$$

$\downarrow$ P/I_2

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-I$$

$\downarrow$ $AgNO_2$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-NO_2$$

$\downarrow$ HO–N=O

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C\begin{matrix}\nearrow NO_2\\ \searrow N=OH\end{matrix}$$

(Pseudinitrol)

$\downarrow$ dil KOH

Blue Colour

3^0 alcohol:

$(CH_3)_3C-OH$

$\downarrow$ P/I_2

$(CH_3)_3C-I$

$\downarrow$ $AgNO_2$

$(CH_3)C-NO_2$

$\downarrow$ HO–N=O

Noreaction

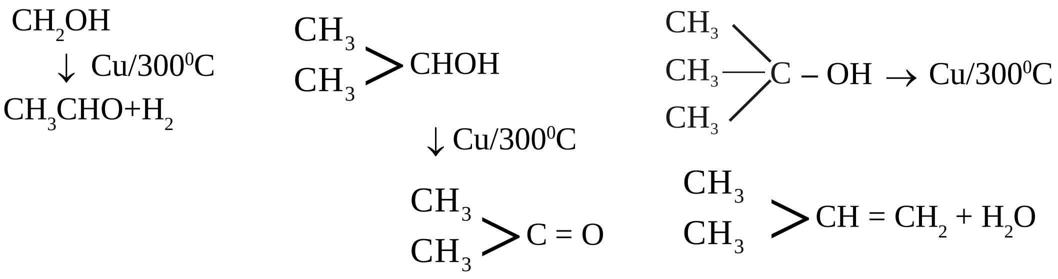
$\downarrow$ dil KOH

No colour

Distinction :

3. Catalytic dehydrogenation

1^0 alcohol **2^0 alcohol** **3^0 alcohol**



1^0 alcohol:

CH_2OH

$\downarrow$ Cu/300^{0}C

CH_3CHO+H_2

2^0 alcohol:

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHOH$$

$\downarrow$ Cu/300^{0}C

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O$$

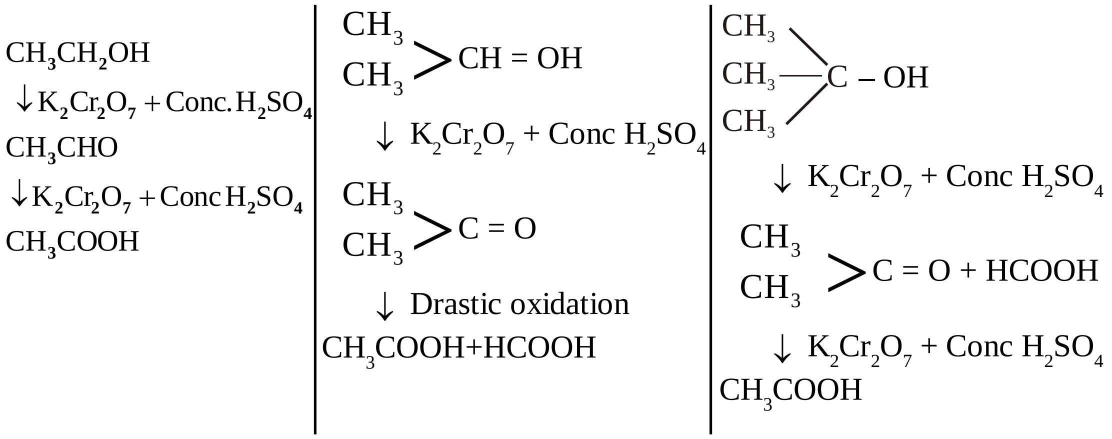
3^0 alcohol:

$$\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!\!-C-OH \rightarrow Cu/300^0C$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH=CH_2+H_2O$$

By oxidation with acidified $K_2Cr_2O_7$Solution

1^0 alcohol **2^0 alcohol** **3^0 alcohol**



1^0 alcohol:

CH_3CH_2OH

$\downarrow K_2Cr_2O_7+Conc.H_2SO_4$

CH_3CHO

$\downarrow K_2Cr_2O_7+Conc\,H_2SO_4$

CH_3COOH

2^0 alcohol:

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH=OH$$

$\downarrow$ $K_2Cr_2O_7$ + Conc H_2SO_4

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O$$

$\downarrow$ Drastic oxidation

$CH_3COOH+HCOOH$

3^0 alcohol:

$$\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!\!-C-OH$$

$\downarrow$ $K_2Cr_2O_7$ + Conc H_2SO_4

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O+HCOOH$$

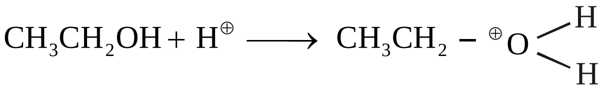
$\downarrow$ $K_2Cr_2O_7$ + Conc H_2SO_4

CH_3COOH

Mechanism of dehydration

The mechanism of dehydration of alcohols to form alkenes occur by the following mechanism.

Step - I : Formation of protonated alcohol - Alcohols react with HCl, H_2SO_4 etc. to form oxonium salt.

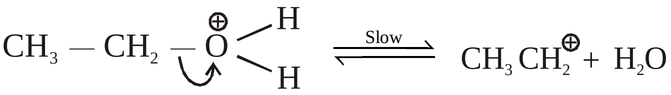


$$CH_3CH_2OH + H^{\oplus} \longrightarrow CH_3CH_2 - {}^{\oplus}O\begin{matrix} H \\ H \end{matrix}$$

(Protonated ethanol)

Step - II : Formation of carbocation

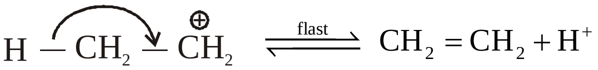
The protonated ethanol readity eliminates a molecule of H_2O to form ethyl carbocation.



$$CH_3 - CH_2 - \overset{\oplus}{O}\begin{matrix} H \\ H \end{matrix} \xrightleftharpoons{\text{Slow}} CH_3\overset{\oplus}{C}H_2 + H_2O$$

This step is slow and hence is the rate determining step of the reaction.

Step - III : Elimination of a proton from the carbocation. The ethyl carbocation readity loses aproton to form ethane.+



$$H - CH_2 - \overset{\oplus}{C}H_2 \xrightleftharpoons{\text{flast}} CH_2 = CH_2 + H^+$$

Lecture - 70

Uses of Methanol -

(i) As a solvent for paints, varnishes etc.

(ii) For manufacture of HCHO used as preservative of biological specimens.

(iii) To prepare methylated spirit.

(iv) As an antifreeze in automobile radiators.

(v) As a substitute for petrol.

Uses of ethanol

(i) A an antiseptic in the form of rectified spirit.

(ii) As a solvent for paints, varnishes, dyes, perfumes etc.

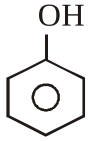
(iii) As an important beverage i.e. beer, rum, whisky, brandy etc.

(iv) As fuel in spirit lamp.

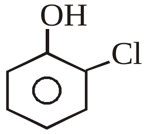
(v) As power alcohol (20% absolute alcohol + 80% petrol with benzene as a cosolvent).

(vi) As antifreeze in automobile radiators.

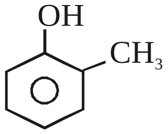
PHENOLS



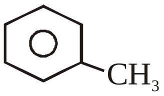
Phenol



o-chlorophenol



o-cresol



m-cresol

(p-cresol)

Preparation of Phenol :

1) From chloro benzene by Dow's process

$$C_6H_5Cl + 2NaOH \xrightarrow{300^0\,C,\ pressure} C_6H_5ONa \xrightarrow{dil\ HCl} C_6H_5OH$$

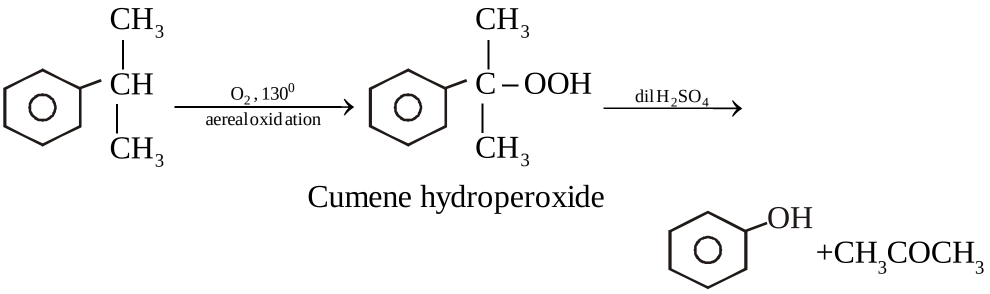
2) From sodium benzene sulphate

$$C_6H_5SO_3Na + 2NaOH \xrightarrow[300^0\,C]{\Delta} C_6H_5ONa(+Na_2SO_3 + H_2O) \xrightarrow{dil\,HCl} C_6H_5OH$$

3) From benzene diazonium chloride

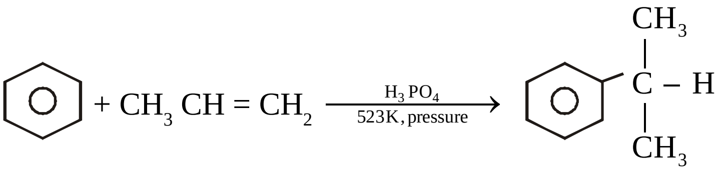
$$C_6H_5N_2^+Cl^- + H_2O \xrightarrow{\Delta} C_6H_5OH + N_2 + HCl$$

4) From Cumene (isopropyl benzene)



Cumene hydroperoxide

N:B Cumere is prepared by Friedel craft alkylation of benzene with propene in presence of phosphoric acid



(Cumene)

Lecture - 71 and 72

Physical and Chemical properties of phenol

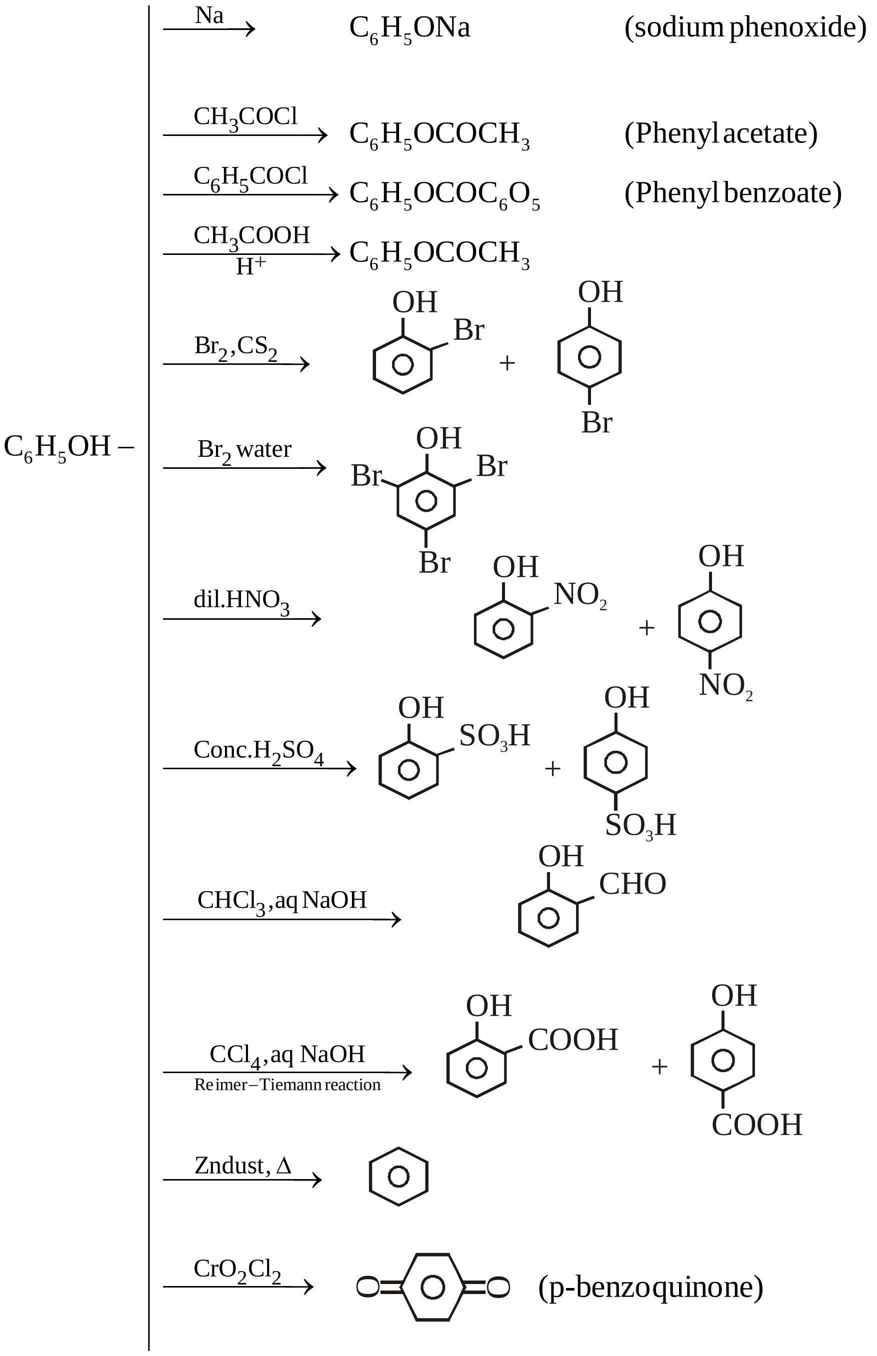
Physical properties :-

(i) Simplest phenol is colourless crystalline solid, soluble in water, due to hydrogen bonding. Other phenols are insoluble in water, but soluble in organic solvents.

The solubility of phenols in water is much lower that wat of alochols because of the larger benzene ring present in their molecule.

2. **Boiling point :** The b.p of phenols are higher in comparison to hydrocarbons, haloarenes of comparable molecular mass due to intermolecular hydrogen bonding between them.

Chemical Properties :- Between phenol and methanol, phenol is more acidic. Phenol is acidic because the phenoxide which is formed by dissociatin is more stable than phenol for which inonization lies to right and free H^+ ion acccounts for acidic nature of phenol.



Uses of Phenol -

(i) As an antiseptic and disinfectant in soaps and lotions.

(ii) Manufacture of drugs like aspirin, salicylic acid, phenacetine.

(iii) In the manufacture of bakelite used into manufacture of electrical goods like switches, plugs etc.

(iv) In the manufacture of picric acid.

(v) Manufacture of azodyes, phenolophthalein indicater.

ETHERS

IUPAC name is alkoxy alkane.

	Common name	IUPAC name
$CH_3OCH_3 \rightarrow$	Dimethyl ether	Methoxy methane
$CH_3OC_2H_5 \rightarrow$	Ethyl methyl ether	Methoxyethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane.
$C_6H_5OCH_2$	Anisole (mithylphonylettor)	Mathoxybenzene

Methods of Preparation

1. Williamsm synthes :- $RX + R'ONa \rightarrow ROR' + NaX.$
2. By dehydration of 1^0 alcohols at 140^0C.

$$CH_3CH_2OH \xrightarrow{Conc.H_2SO_4} CH_3CH_2HSO_4 \xrightarrow[140^0C]{} CH_3 - CH_2OH \qquad CH_3-CH_2O-CH_2-CH_3 + H_2O.$$

3. By catalytic dehydration of alcohols

$$CH_3CH_2OH + HOCH_2CH_3 \xrightarrow[513-523k]{Al_2O_3} CH_3CH_2OCH_2CH_3 + H_2O$$

4. From alkylhalide - By boiling alkyl halides with dry silveroxide.

$$2R - I + Ag_2O \rightarrow R - O - R + 2AgI$$

5. By action of diazomethane on alcohol.

$$CH_3CH_2OH + CH_2N_2 \xrightarrow{HBF_4} CH_3CH_2OCH_3 + N_2$$

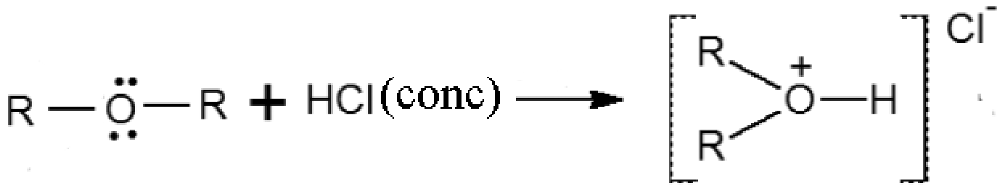
Lecture - 73

Physical Properties of Ethers -

1. Dimethyl ether and diethyl ethers are gases at ordinary temperature
2. **Boiling point -** B.P. of ethers are much lower than those of isomeric alcohols. It is because unlike alcohols, ethers donot form hydrogen bonds.
3. **Solubility -** Ethers containing upto three carbon atoms are soluble in water due to hydrogen bonding with water.

Chemical Properties

1. Ethers react with acids to form oxonium salts.



Dialkyl oxonium chloride

2. **Reactions involving the cleavage of Carbon-oxygen bond**

(a) Reaction with halogen acid to give alkyl halide

$$R-O-R+HX\xrightarrow{373K}RX+ROH$$

$$R-O-R+\underset{(excess)}{2HI}\xrightarrow{373K}2RI+H_2O$$

$$C_6H_5OR+HX\rightarrow C_6H_5OH+R-X$$

$$C_6H_5CH_3+HI\rightarrow C_6H_5OH+CH_3I.$$

(b) **Hydrolysis** - $R-O-R+H_2O\xrightarrow[Pressure]{dilH_2SO_4}\Delta 2ROH$

(c) Action with conc. H_2SO_4

$$C_2H_5OC_2H_5\xrightarrow[\Delta]{Conc.H_2SO_4}C_2H_5OH+C_2H_5HSO_4$$

(d) Action with PCl_5

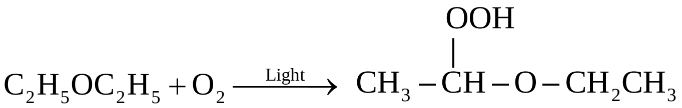
$$C_2H_5OC_2H_5+PCl_5\rightarrow 2C_2H_5Cl+POCl_3$$

(e) Action with acid chloride to formester

$$C_2H_5OC_2H_5+CH_3COCl\xrightarrow[\Delta]{anti.ZnCl_2}C_2H_5Cl+CH_3COOC_2H_5.$$

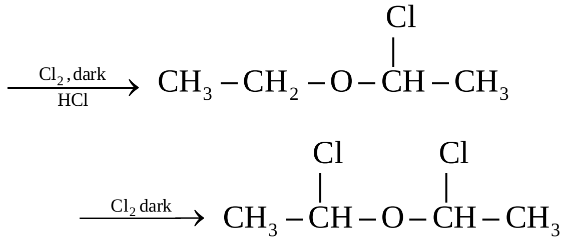
3. **Reaction involing alkyl group**

(a) Action of air and light - On exposure to air and light ether is oxidised to peroxides.



$$C_2H_5OC_2H_5+O_2\xrightarrow{Light}CH_3-\overset{\overset{\displaystyle OOH}{|}}{CH}-O-CH_2CH_3$$

(b) Halogenation : $CH_3CH_2OCH_2CH_3$

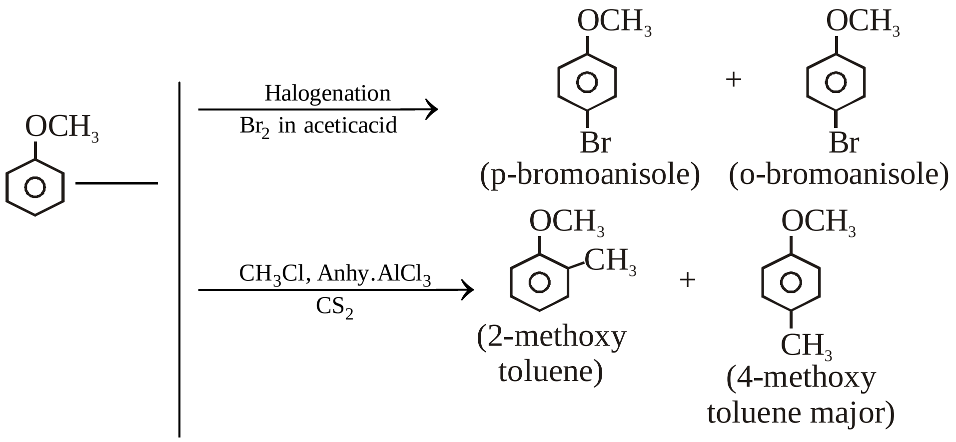


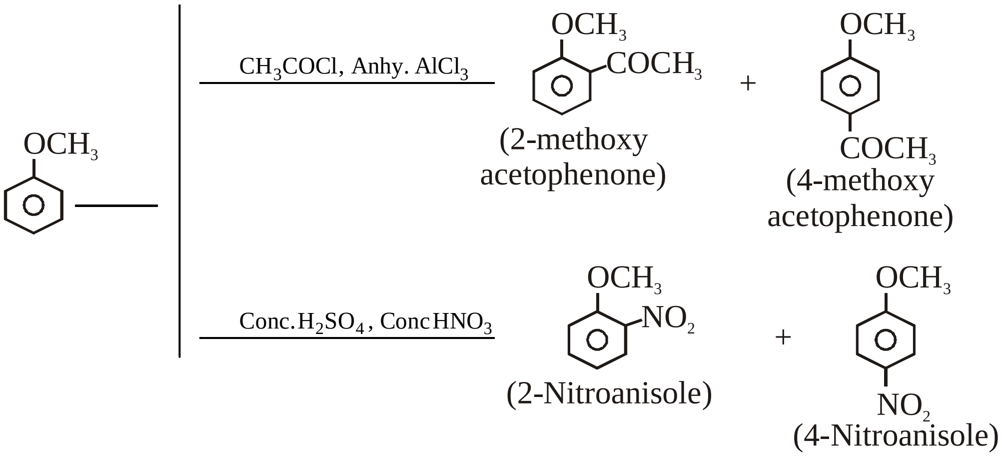
$$\xrightarrow[HCl]{Cl_2,dark}CH_3-CH_2-O-\overset{\overset{\displaystyle Cl}{|}}{CH}-CH_3$$

$$\xrightarrow{Cl_2\,dark}CH_3-\overset{\overset{\displaystyle Cl}{|}}{CH}-O-\overset{\overset{\displaystyle Cl}{|}}{CH}-CH_3$$

$\alpha,\alpha^{/}$ - Dicholoro ethyl ether

4. **Electrophilic substitution reactions** In aromatic ethers the aloxy group is ortho and p-directing and because of inductive effect, the alxoxy group activates the aromatic ring towards electrophilic substitution reactions.





Lecture - 74, 75 & 76

UNIT - XII

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

	Common name		**IUPAC name**
HCHO	Formaldehyde		Methanal
CH_3CHO	Acetaldehyde		Ethanal
$\begin{matrix}CH_3\\CH_3\end{matrix}\Big\rangle C=O$	Acetone		propanone
C_6H_5-CHO	Benzal dehyde	IUPAC approved name	(benzenecarbaldehyde)
$C_6H_5COCH_3$	Acetophenone		(Phenylethanone)
$C_6H_5COC_6H_5$	Benzophenone		(Diphenylmethanone)

Methods of Preparation

1. By oxidation of 1^0 and 2^0 alcohols aldehydes and ketones are formed respectively.

$$RCH_2OH \xrightarrow[\text{(or) PCC or collin's reagent}]{K_2Cr_2O_7+Conc.H_2SO_4} RCHO$$

$$\begin{matrix}R\\R\end{matrix}\Big\rangle CHOH \xrightarrow{K_2Cr_2O_7+Conc.H_2SO_4} \begin{matrix}R\\R\end{matrix}\Big\rangle C=O$$

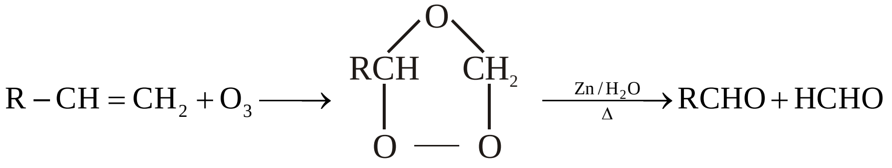
2. By catalytic dehydrogenation of alochols

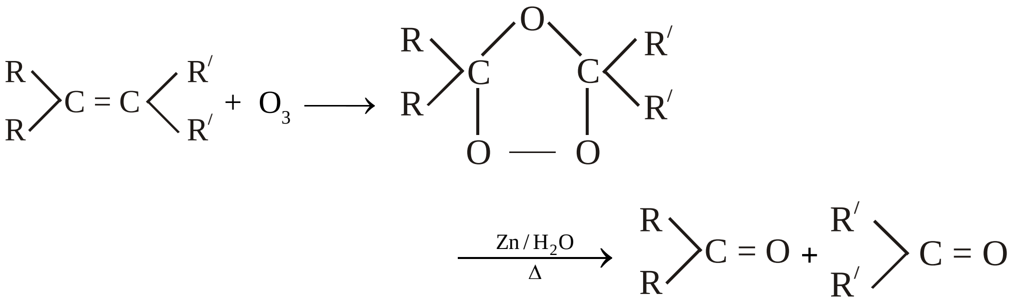
$$RCH_2OH \xrightarrow{Cu/300^0C} RCHO + H_2$$

$$\begin{matrix}R\\R\end{matrix}\Big\rangle CHOH \xrightarrow{Cu/300^0C} \begin{matrix}R\\R\end{matrix}\Big\rangle C=O + H_2$$

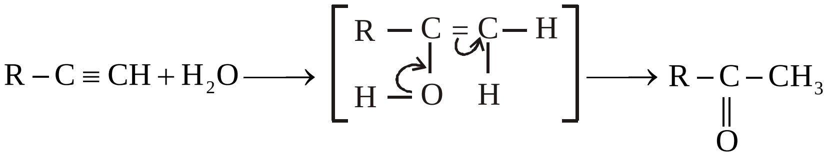
3. From alkenes and alkynes.

(i) By ozonolysis of alkenes.

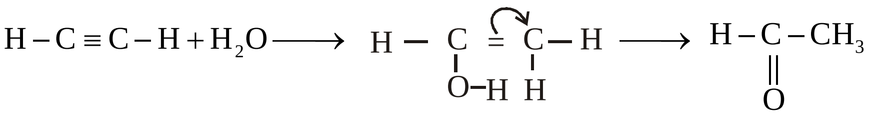




(ii) By hydration of alkynes in presence of dil. H_2SO_4 and $HgSO_4$ at 60^0C.



(ketone)



(acetaldehyde)

4. By distillation of Ca-salt of fatty acids.

(a) $HCOOCa/2 + HCOOCa/2 \xrightarrow{\text{Dry distillation}} CaCO_3 + HCHO$,

$$\begin{array}{l} HCOO^- \\ \quad\quad\quad Ca^{2+} \longrightarrow HCHO + CaCO_3 \\ HCOO^- \end{array}$$

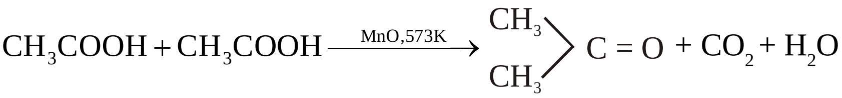
$HCOOCa/2 + RCOOCa/2 \xrightarrow{\text{Dry distillation}} CaCO_3 + RCHO$

$RCOOCa/2 + RCOOCa/2 \xrightarrow{\text{Dry distillation}} CaCO_3 + RCOCH_3$

5. **From carboxylic acids**

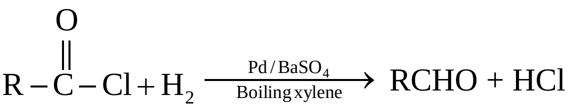
$HCOOH + HCOOH \xrightarrow{\text{MnO,573K}} HCHO + CO_2 + H_2O$

$HCOOH + CH_3COOH \xrightarrow{\text{MnO,573K}} CH_3CHO + CO_2 + H_2O$



$$CH_3COOH + CH_3COOH \xrightarrow{\text{MnO,573K}} (CH_3)_2C=O + CO_2 + H_2O$$

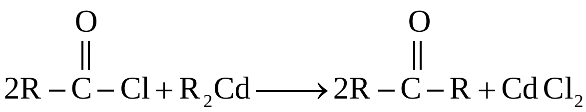
6. **From Acid Chloride**



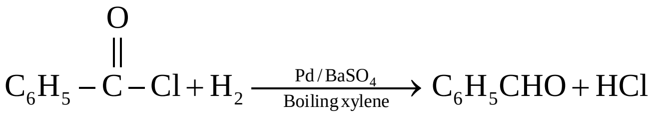
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + H_2 \xrightarrow[\text{Boiling xylene}]{Pd/BaSO_4} RCHO + HCl$$

This reaction is called Rosenmund's reduction.

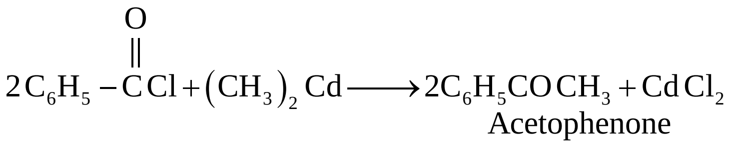
Ketones are prepared by the action of dialkyl cadmium.



$$2R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + R_2Cd \longrightarrow 2R-\overset{\overset{\displaystyle O}{\|}}{C}-R + CdCl_2$$



$$C_6H_5-\overset{\overset{\Large O}{\|}}{C}-Cl+H_2\xrightarrow[\text{Boiling xylene}]{Pd/BaSO_4}C_6H_5CHO+HCl$$

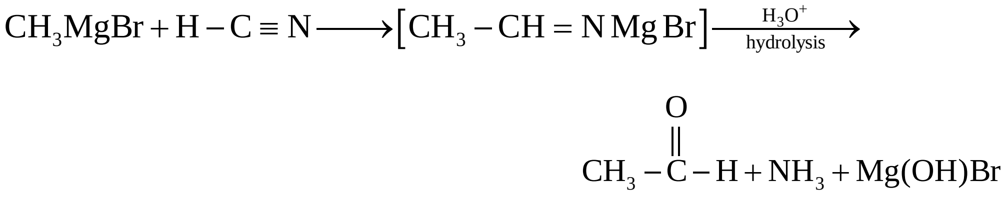


$$2C_6H_5-\overset{\overset{\Large O}{\|}}{C}Cl+(CH_3)_2Cd\longrightarrow\underset{\text{Acetophenone}}{2C_6H_5COCH_3}+CdCl_2$$

7. **From Grignard's reagent**

Preparation of aldehydes-

When Grignards reagent reacts with HCN and the product is hydrolysed aldehyde is formed.

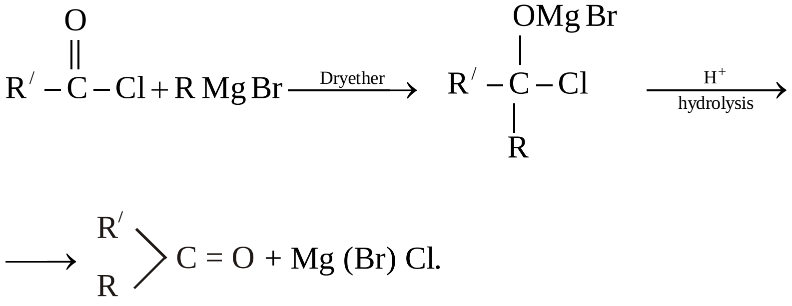


$$CH_3MgBr+H-C\equiv N\longrightarrow[CH_3-CH=NMgBr]\xrightarrow[\text{hydrolysis}]{H_3O^+}$$

$$CH_3-\overset{\overset{\Large O}{\|}}{C}-H+NH_3+Mg(OH)Br$$

Preparation of ketone from Grignard reagent

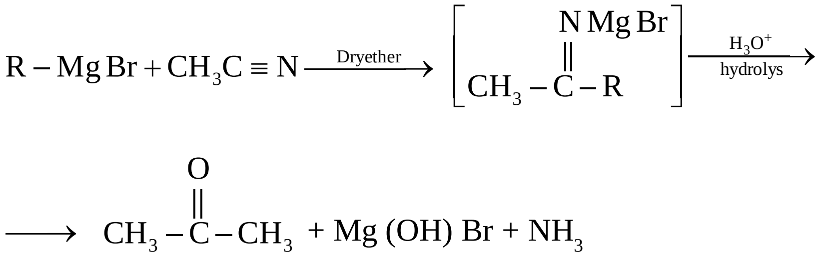
(a)



$$R^/-\overset{\overset{\Large O}{\|}}{C}-Cl+RMgBr\xrightarrow{\text{Dryether}}R^/-\underset{\underset{\Large R}{|}}{\overset{\overset{\Large OMgBr}{|}}{C}}-Cl\xrightarrow[\text{hydrolysis}]{H^+}$$

$$\longrightarrow\begin{matrix}R^/\\R\end{matrix}\Big\rangle C=O+Mg(Br)Cl.$$

(b)



$$R-MgBr+CH_3C\equiv N\xrightarrow{\text{Dryether}}\left[CH_3-\overset{\overset{\Large NMgBr}{\|}}{C}-R\right]\xrightarrow[\text{hydrolys}]{H_3O^+}$$

$$\longrightarrow CH_3-\overset{\overset{\Large O}{\|}}{C}-CH_3+Mg(OH)Br+NH_3$$

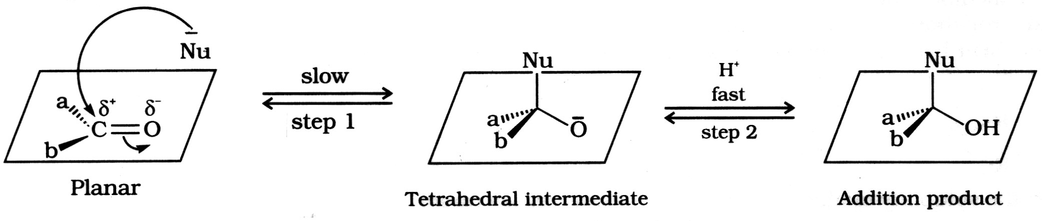
Properties of Aldehydes & ketones

Physical properties (1) lower members are soluble in water due to hydrogen bonding and solubility decreases with increase in molecular mass. All aldehydes & ketones are soluble in organic solvents like alcohol, ether etc.

2. **Boiling point -** B.P. of aldehydes and ketones are more than those of alkanes but less than those of alcohols of comparable molecular mass.

1. Nucleophitic addition Reactions since aldehydes and ketones both possess the carbonyl group, they undergo nucleophilic addition reactions.

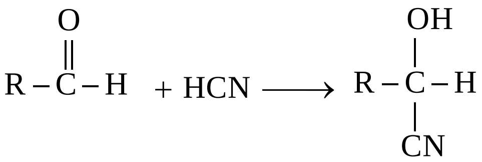
Mechanism. A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approxomately perpendicular to the plane of sp^2 hydroxidised orbitals of carbonyl carbon. The hydroxidisation of carbon changes from sp^2 to sp^3 in this process and a tetrahedral alkoxide intermediate is formed. This intermediate captures a proton from the reaction medium to give the neutral product. The net result is addition of Nu^- and H^+ across the carbon oxygen double bond as shown in the figure.



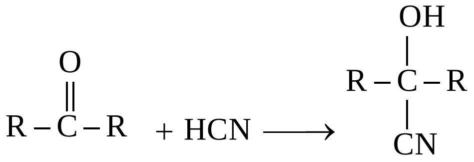
Nucleophilic attack on carbonyl carbon

Examples :

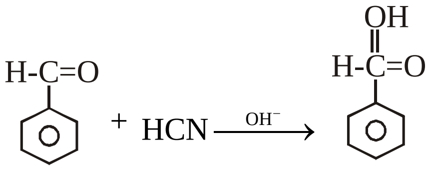
1. Add. of HCN to form corresponding cyanohydrin.



$$R-\overset{\overset{\large O}{||}}{C}-H + HCN \longrightarrow R-\underset{\underset{\large CN}{|}}{\overset{\overset{\large OH}{|}}{C}}-H$$

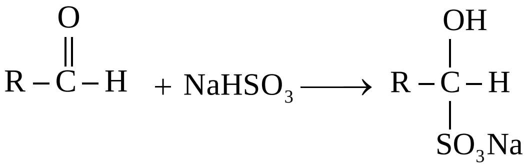


$$R-\overset{\overset{\large O}{||}}{C}-R + HCN \longrightarrow R-\underset{\underset{\large CN}{|}}{\overset{\overset{\large OH}{|}}{C}}-R$$

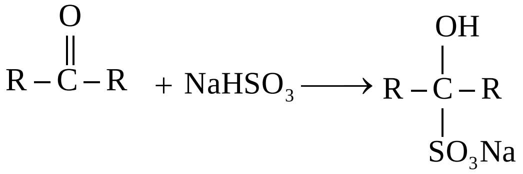


Benzaldehyde-Cyanohydrin

2. Addition of $NaHSO_3$ to form corresponding crystalline bisulphite compound.

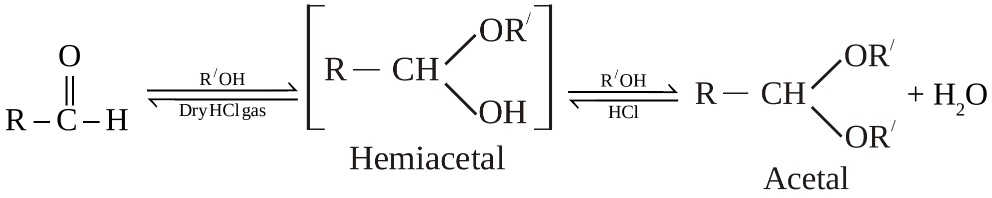


$$R-\overset{\overset{\large O}{||}}{C}-H + NaHSO_3 \longrightarrow R-\underset{\underset{\large SO_3Na}{|}}{\overset{\overset{\large OH}{|}}{C}}-H$$

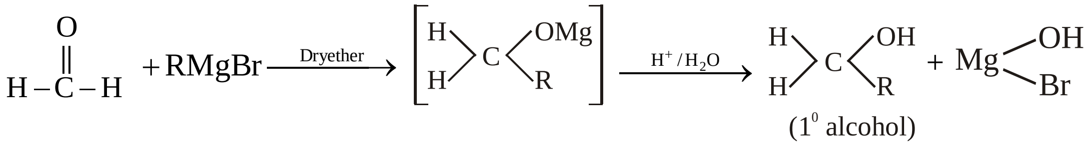


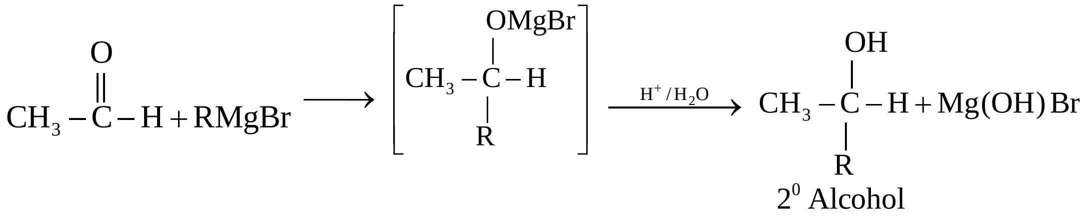
$$R-\overset{\overset{\large O}{||}}{C}-R + NaHSO_3 \longrightarrow R-\underset{\underset{\large SO_3Na}{|}}{\overset{\overset{\large OH}{|}}{C}}-R$$

(c) **Reaction with alocohol** - Aldehydes react with one equivalent of monohydric alcohol in presence of dry HCl to give hemiacetal (alkoxy alcohol) which further react with one more molecule of alcohol to give acetal.



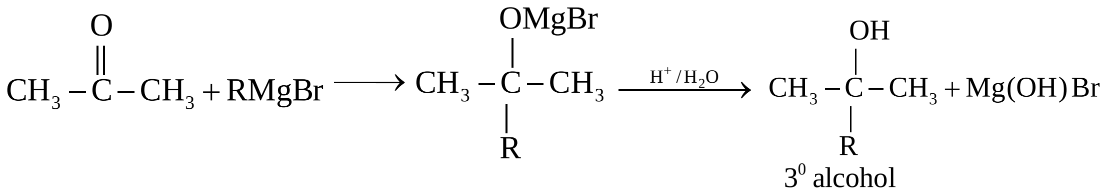
(d) Addition of Grignard's reagent





$$CH_3-\overset{\overset{\large O}{\|}}{C}-H+RMgBr \longrightarrow \left[CH_3-\underset{\underset{\large R}{|}}{\overset{\overset{\large OMgBr}{|}}{C}}-H\right] \xrightarrow{H^+/H_2O} CH_3-\underset{\underset{\large R}{|}}{\overset{\overset{\large OH}{|}}{C}}-H+Mg(OH)Br$$

2^0 Alcohol

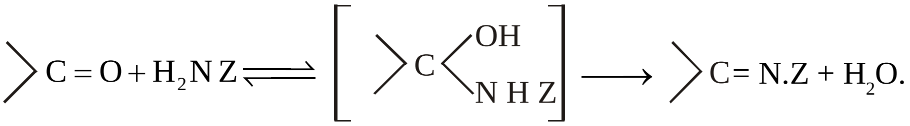


$$CH_3-\overset{\overset{\large O}{\|}}{C}-CH_3+RMgBr \longrightarrow CH_3-\underset{\underset{\large R}{|}}{\overset{\overset{\large OMgBr}{|}}{C}}-CH_3 \xrightarrow{H^+/H_2O} CH_3-\underset{\underset{\large R}{|}}{\overset{\overset{\large OH}{|}}{C}}-CH_3+Mg(OH)Br$$

3^0 alcohol

(e) Addition of ammonia derivatives (Addition - elmination)

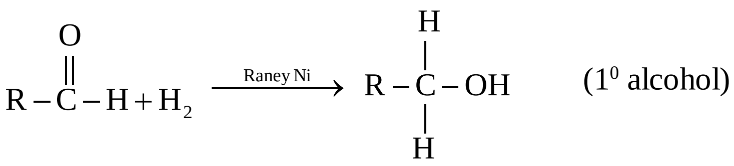
($H_2N – Z$, where z = alkyl, aryl, OH, NH_2 , C_6H_5NH, $NHCONH_2$)



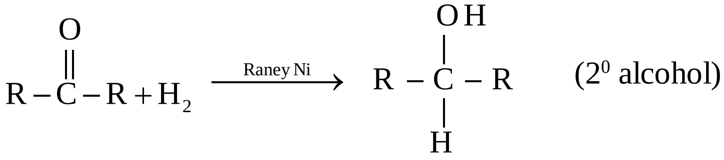
Hence by reaction with hydroxyl amine, hydrazine, phenyl hydrazine and semicarbozide corresponding oxime, hydrazone, phenyl hydrazone and semicarbazones are formed. The reaction is carried out in controlled pH medium.

2. **Reduction**

(a) Catalytic reduction - Aldehydes and ketones are reduced catalytically by H_2 in presence of Raney nickel, Pt or Pd to give 1^0 and 2^0 alcohols respectively.



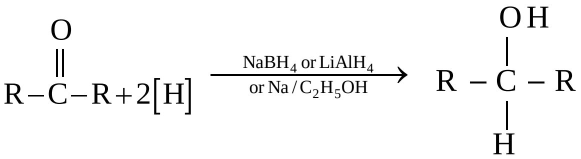
$$R-\overset{\overset{\large O}{\|}}{C}-H+H_2 \xrightarrow{\text{Raney Ni}} R-\underset{\underset{\large H}{|}}{\overset{\overset{\large H}{|}}{C}}-OH \quad (1^0 \text{ alcohol})$$



$$R-\overset{\overset{\large O}{\|}}{C}-R+H_2 \xrightarrow{\text{Raney Ni}} R-\underset{\underset{\large H}{|}}{\overset{\overset{\large OH}{|}}{C}}-R \quad (2^0 \text{ alcohol})$$

(b) Reduction by chemical reducing agents

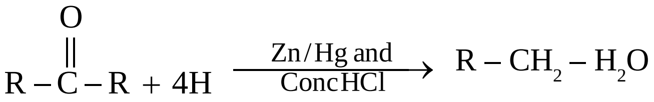
$$R-CHO+2[H]\xrightarrow{NaBH_4 \text{ or } LiAlH_4} RCH_2OH$$



$$R-\overset{\overset{O}{\|}}{C}-R+2[H]\xrightarrow[\text{or } Na/C_2H_5OH]{NaBH_4 \text{ or } LiAlH_4} R-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-R$$

(C) (i) Reduction to alkanes by Zinc amalgan and Conc. HCl

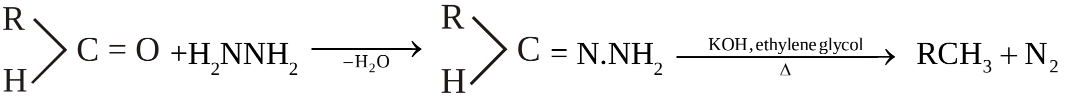
$$R-CHO+4H\xrightarrow[\text{Conc HCl}]{Zn/Hg \text{ and}} R-CH_3+H_2O$$



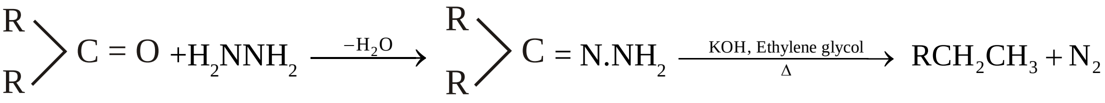
$$R-\overset{\overset{O}{\|}}{C}-R+4H\xrightarrow[\text{Conc HCl}]{Zn/Hg \text{ and}} R-CH_2-H_2O$$

This reaction is called Clemmenson reduction.

(C) (i) Reduction to Alkane by hydrazine followed by heating with NaOH or KOH in presence of ethylene glycol. This reaction is called Wolff Kishner reduction.

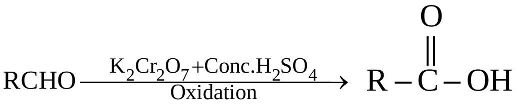


$$\begin{matrix}R\\H\end{matrix}\!>C=O+H_2NNH_2\xrightarrow[-H_2O]{}\begin{matrix}R\\H\end{matrix}\!>C=N.NH_2\xrightarrow[\Delta]{KOH,\text{ ethylene glycol}}RCH_3+N_2$$

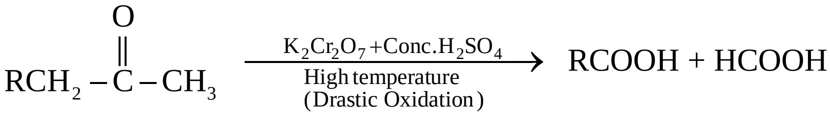


$$\begin{matrix}R\\R\end{matrix}\!>C=O+H_2NNH_2\xrightarrow{-H_2O}\begin{matrix}R\\R\end{matrix}\!>C=N.NH_2\xrightarrow[\Delta]{KOH,\text{ Ethylene glycol}}RCH_2CH_3+N_2$$

3. Oxidation



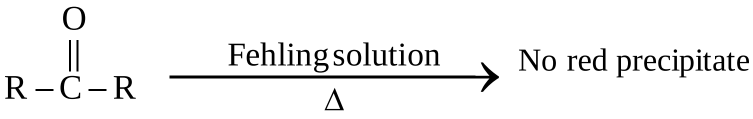
$$RCHO\xrightarrow[\text{Oxidation}]{K_2Cr_2O_7+Conc.H_2SO_4}R-\overset{\overset{O}{\|}}{C}-OH$$



$$RCH_2-\overset{\overset{O}{\|}}{C}-CH_3\xrightarrow[\substack{\text{High temperature}\\(\text{Drastic Oxidation})}]{K_2Cr_2O_7+Conc.H_2SO_4}RCOOH+HCOOH$$

(ii) Test with Fehling solution : Fehling solution is the mixture of equal amount of Fehling A (Aqueous $CuSO_4$ solution) and Fehling B (aqueous sodium potassium tartrate).

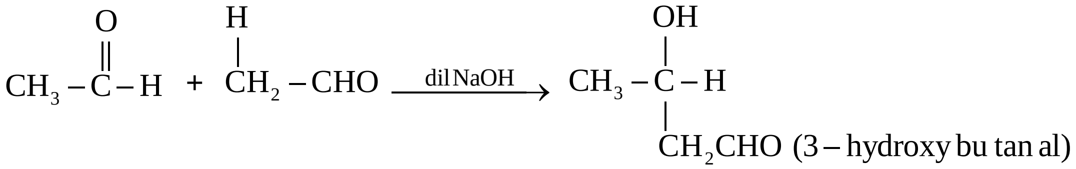
$$RCHO+2Cu^{2+}+5OH^-\xrightarrow{\text{heat}}RCOO^-+\underset{(\text{Red ppt})}{Cu_2O}+3H_2O$$



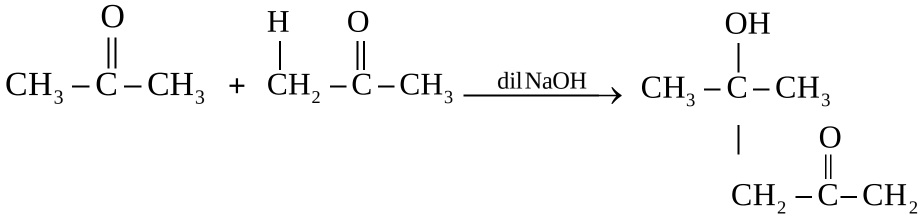
$$R-\overset{\overset{O}{\|}}{C}-R\xrightarrow[\Delta]{\text{Fehling solution}}\text{No red precipitate}$$

4. **Reaction due to $\alpha-$hydrogen**

(i) **Aldol condensation -** Aldehydes & ketones having atleast one $\alpha-$hydrogen undergo reaction in presence of dilute NaOH to form $\beta-$ hydroxy aldehydes (aldol) and $\beta-$hydroxy ketones (ketol) respectively. This reaction is called aldol condensation.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + \overset{\overset{\displaystyle H}{|}}{C}H_2-CHO \xrightarrow{\text{dil NaOH}} CH_3-\underset{\underset{\displaystyle CH_2CHO}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-H \text{ (3-hydroxybutanal)}$$



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + \overset{\overset{\displaystyle H}{|}}{C}H_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{\text{dil NaOH}} CH_3-\underset{\underset{\displaystyle CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3$$

(4-hydroxy-4-methyl pentan-2-one)

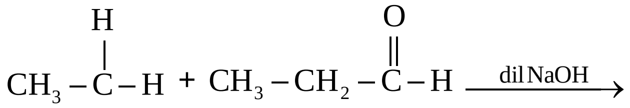
5. **Connizzaro reaction :-** Aldehydes having no $\alpha-$hydrogen atom undergo self oxidation and reduction on heating with conc. NaOH

$$2HCHO \xrightarrow{\text{conc. NaOH}} HCOONa + CH_3OH$$

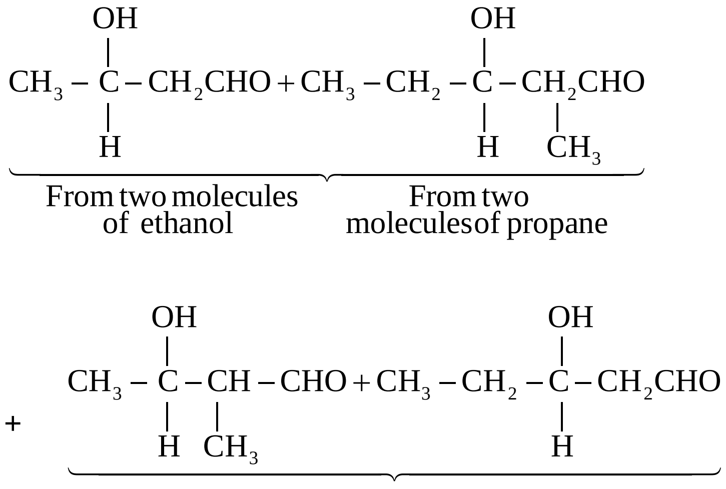
$$2C_6H_5CHO \xrightarrow{\text{Conc. NaOH}} C_6H_5COONa + C_6H_5CH_2OH$$

6. **Crossed - Aldol Condensation :-** When aldol condensation takes place between two different aldehydes and / or ketones, it is called cross aldol condensation. If both of them contain $\alpha-$hydrogen atoms, it gives a mixture of four products.

Example -



$$CH_3-\overset{\overset{\displaystyle H}{|}}{C}-H + CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{\text{dil NaOH}}$$

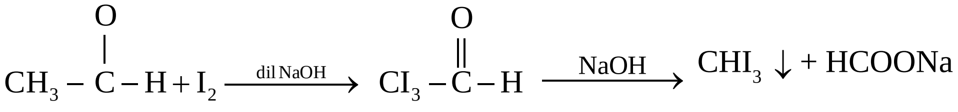


$$\underbrace{CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_2CHO}_{\text{From two molecules of ethanol}} + \underbrace{CH_3-CH_2-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-\underset{\underset{\displaystyle CH_3}{|}}{C}H_2CHO}_{\text{From two molecules of propane}}$$

$$+ \underbrace{CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CHO + CH_3-CH_2-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_2CHO}$$

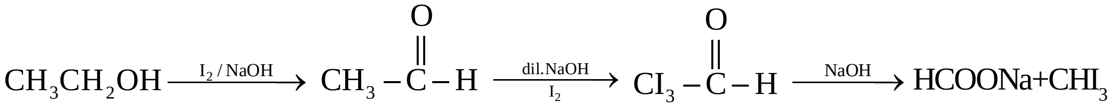
From one molecule of ethanal and one molecule of propanal
(Crossed aldol product)

7. **Iodoform reactions :-** Compounds containing acetyl group $CH_3–CO^-$ or any compound which on oxidation contains acetyl group under go iodoform reaction when treated with I_2 and dil NaOH.

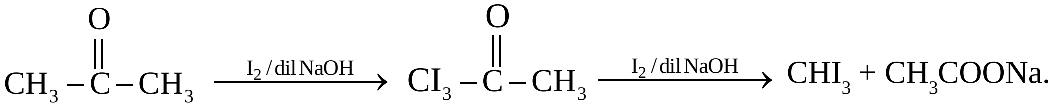


$$CH_3-\overset{\overset{O}{|}}{C}-H+I_2\xrightarrow{\text{dil NaOH}}CI_3-\overset{\overset{O}{\|}}{C}-H\xrightarrow{\text{NaOH}}CHI_3\downarrow+HCOONa$$

iodoform (yellow ppt)



$$CH_3CH_2OH\xrightarrow{I_2/NaOH}CH_3-\overset{\overset{O}{\|}}{C}-H\xrightarrow[I_2]{\text{dil.NaOH}}CI_3-\overset{\overset{O}{\|}}{C}-H\xrightarrow{\text{NaOH}}HCOONa+CHI_3$$



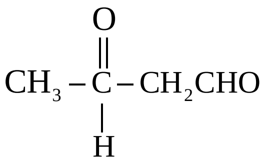
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3\xrightarrow{I_2/\text{dil NaOH}}CI_3-\overset{\overset{O}{\|}}{C}-CH_3\xrightarrow{I_2/\text{dil NaOH}}CHI_3+CH_3COONa.$$

Lecture - 77

Distinction between aldehydes & ketones

Aldehydes	**Ketones**
1. **Oxidation :**	**1. Oxidation :-**
(a) Aldehydes are easily oxidised by oxidising agents like acidified $K_2Cr_2O_7$ solution to give corresponding acids containing same number of carbon atoms as the aldehydes $CH_3CHO\xrightarrow{K_2Cr_2O_7+Conc.H_2SO_4}CH_3COOOH$	**(a)** Ketones are not easily oxidised, but under drastic condition in presence of acidified $K_2Cr_2O_7$ solution are oxidised to give a mixture of carboxylic acids each containing less number of carbon atoms than the ketone. $\text{Acetone}\xrightarrow[\text{Drastic oxidation}]{K_2Cr_2O_7+Conc.H_2SO_4}CH_3COOH+HCOOH$
(b) Oxidation by Tollen's reagent $RCHO+2\left[Ag(NH_3)_2\right]+2OH^-\xrightarrow{\Delta}$ $RCOO^-+2Ag+2H_2O+4NH_3$ (Silver mirror)	(b) $RCOR\xrightarrow[\Delta]{\text{Tollen's reagent}}$ No silver mirror
(c) **Oxidation by Fehling solution** $RCHO+2Cu^{2+}+5OH^-\xrightarrow{\text{heat}}RCOO^-$ $+Cu_2O+3H_2O(\text{Red ppt})$	(c) $RCOR\xrightarrow[\Delta]{\text{Fehling solution}}$ No red precipitate

Distinction between acetaldehyde and formal dehyde

Formaldehyde	Acetaldehyde
(1) Aldol condensation- It does not not under go aldol condensation as it does not contain $\alpha - \text{H}$ atom	**(1) Aldol condensation** $2CH_3CHO \xrightarrow{\text{dil NOOH}}$  $CH_3 - \underset{\substack{\vert \\ H}}{\overset{\substack{O \\ \Vert}}{C}} - CH_2CHO$ (Acetaldol)
(2) **Cannizzaro's reaction** $HCHO + HCHO \xrightarrow{\text{Conc. NaOH}} HCOONa + CH_3\,CH_2OH$ It responds as containing $\alpha - \text{H}$ atom	(2) **Cannizzaro's reaction** $CH_3CHO \xrightarrow{\text{Conc. NaOH}}$ NO reaction as CH_3CHO contains $\alpha - \text{H}$ atom
(3) It does not contain $\left(\overset{\substack{O \\ \Vert}}{-C} - CH_3\right)$ group. $HCHO + I_2 \xrightarrow{\text{dil NaOH}}$ No idoform is formed.	(3) **Iodoform test:** It contains $\left(\overset{\substack{O \\ \Vert}}{-C} - CH_3\right)$ group so idoform is formed $CH_3CHO \xrightarrow{I_2/NaOH} CHI_3 + HCOONa$ (yellow ppt) (Laboratory test)

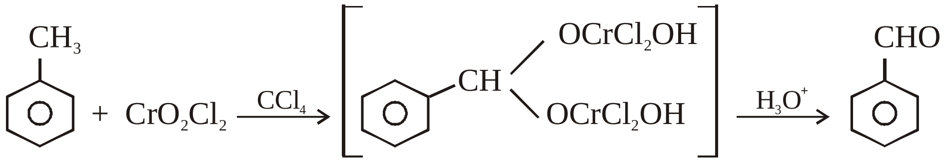
Iodoform test is the laboratory test to distinguish HCHO from CH_3CHO.

Lecture - 78

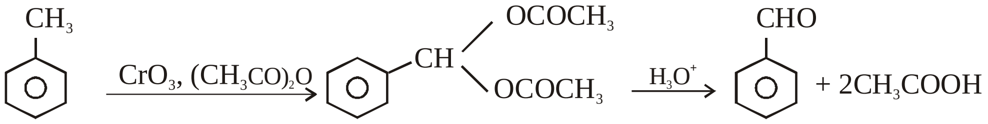
Aromatic Aldehydes

Preparation

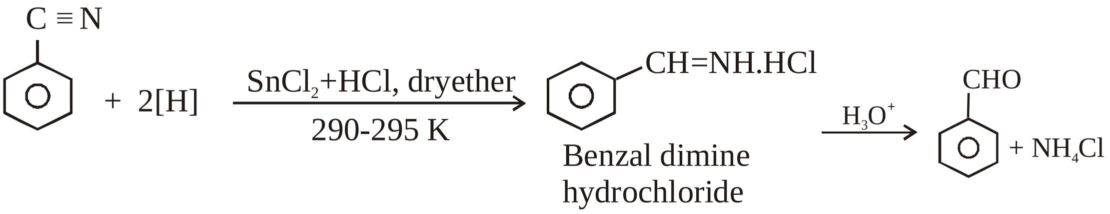
(1) By Etard's reaction



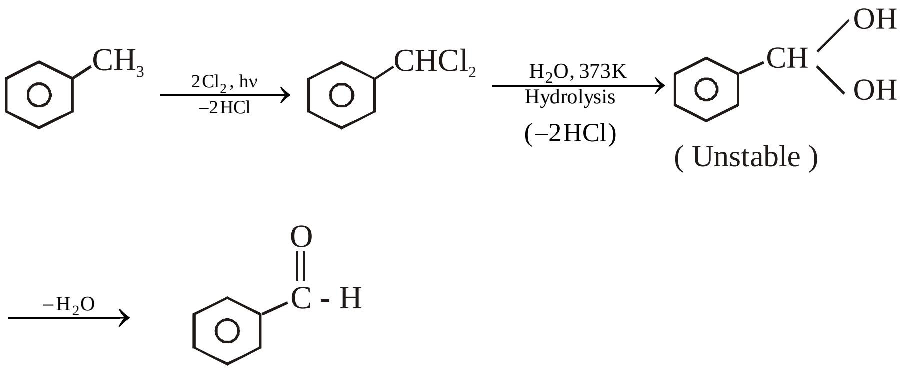
(2) By oxidation of toluene by chromium trioxide in acetic anhydride followed by hydrolysis.



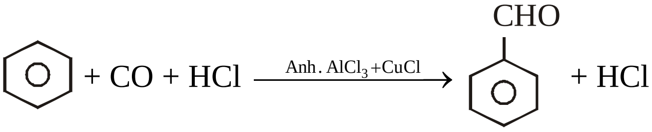
(3) From benzonitrile



(4) By side chain halogenation toluene followed by hydrolysis.



(5) By Gatterman – Koch reaction



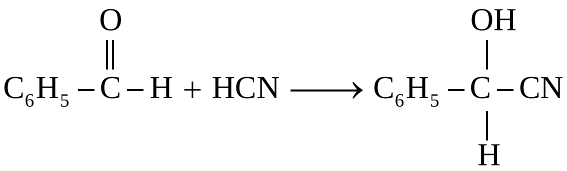
(6) By Rosenmund’s reduction

$$C_6H_5COCl + H_2 \xrightarrow[\text{Ouinolin}]{Pd/BaSO_4} C_6H_5CHO + HCl$$

Lecture - 79

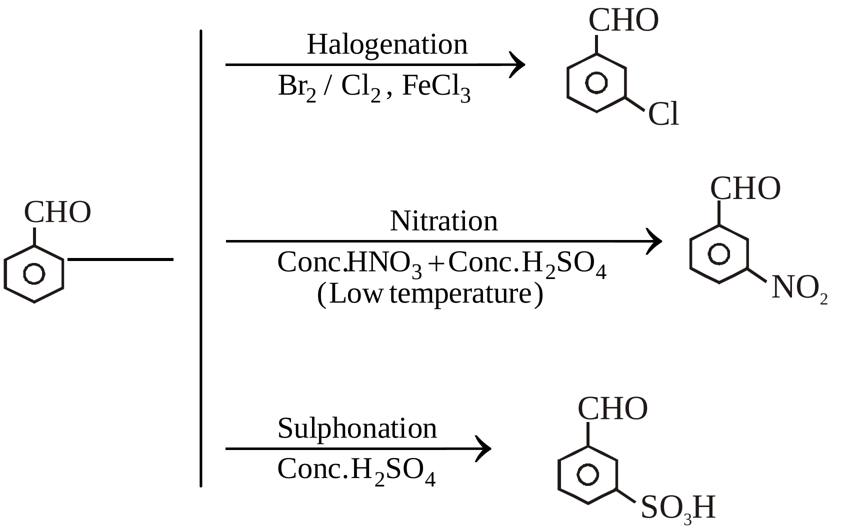
Properties of Benzaldehyde

(1) (i) Reaction with HCN to form benzaldehyde cyanohydrin



$$C_6H_5-\overset{\overset{O}{\|}}{C}-H + HCN \longrightarrow C_6H_5-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CN$$

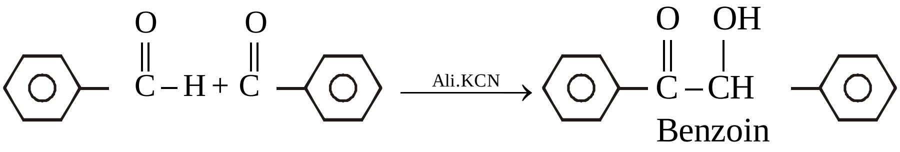
(2) Electrophilic substitution reactions :



(m-formyl benzene sulphoric acid)

(3) Reaction with alcoholic KCN :

Two molecules of benzaldehyde uner go condensation to give benzoine. This reaction is called benzoin condensation.



(4) Benzaldehyde reacts with 10 amines in presence of acides catalyst to form Schiff's base.

$$C_6H_5CHO + C_6H_5NH_2 \xrightarrow{H^+, Heat} C_6H_5 - CH = N C_6H_5 + H_2O$$

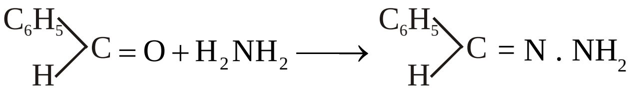
Benzal aniline

(A Schiff 's nase)

(5) Cannizzaro's reaction

$$C_6H_5CHO + C_6H_5CHO \xrightarrow{Conc\,NaOH} C_6H_5COONa + C_6H_5CH_2OH$$

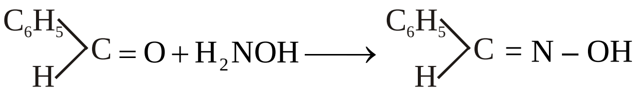
(6) Reaction with hydrazine



$$\left.\begin{matrix}C_6H_5\\H\end{matrix}\right\rangle C = O + H_2NH_2 \longrightarrow \left.\begin{matrix}C_6H_5\\H\end{matrix}\right\rangle C = N . NH_2$$

benzaldehyde hydrazone

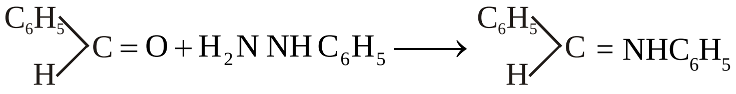
(7) Reaction with hydroxylamine



$$\left.\begin{matrix}C_6H_5\\H\end{matrix}\right\rangle C = O + H_2NOH \longrightarrow \left.\begin{matrix}C_6H_5\\H\end{matrix}\right\rangle C = N - OH$$

benzaldehyde oxime

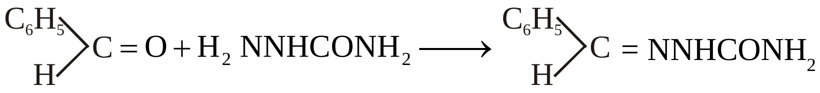
(8) **Reaction with Phenylhydrazine-**



$$\begin{matrix}C_6H_5\\H\end{matrix}\!\!>C=O+H_2N\,NH\,C_6H_5\longrightarrow\begin{matrix}C_6H_5\\H\end{matrix}\!\!>C=NHC_6H_5$$

(Phenyl hydrazone)

(9) **Reaction with semicarbozide**

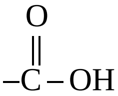


$$\begin{matrix}C_6H_5\\H\end{matrix}\!\!>C=O+H_2\;NNHCONH_2\longrightarrow\begin{matrix}C_6H_5\\H\end{matrix}\!\!>C=NNHCONH_2$$

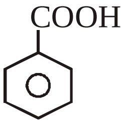
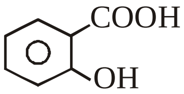
(semicarbazone)

Lecture - 80

MONOCARBOXYLIC ACIDS -



Organic compounds containing $-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ (carboxyl group) are called carboxylic acid.

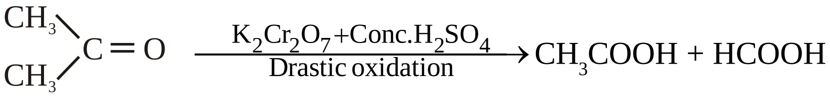
	Common name	**IUPAC**
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
 -	Benzoic acid	
 -	Salicylic acid	

Preparation

(1) By oxidation of alcohols, aldehydes and ketones

$$RCH_2OH\xrightarrow{K_2Cr_2O_7+Conc.H_2SO_4}RCHO\xrightarrow{K_2Cr_2O_7+Conc.H_2SO_4}RCOOH$$

$$RCHO\xrightarrow{K_2Cr_2O_7+Conc.H_2SO_4}RCOOH$$



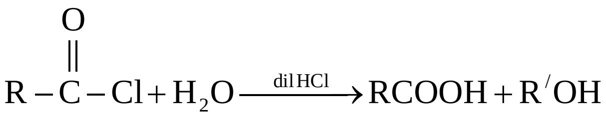
$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O\xrightarrow[\text{Drastic oxidation}]{K_2Cr_2O_7+Conc.H_2SO_4}CH_3COOH+HCOOH$$

(Acetone)

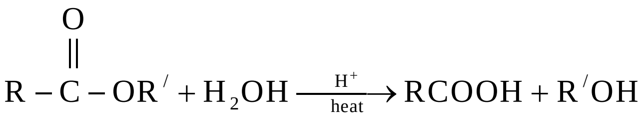
(2) Hydrolysis of alkyl cyanide

$$RCN+2H_2O+HCl\xrightarrow[\Delta]{}RCOOH+NH_4Cl$$

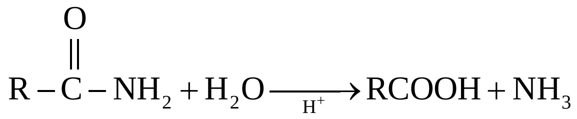
(3) By hydrolysis of acid chloride, ester, acid amide, and anhydride.



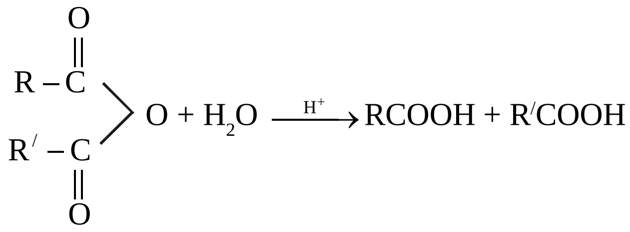
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl+H_2O\xrightarrow{dil\,HCl}RCOOH+R'OH$$



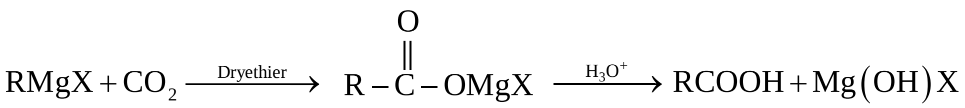
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR'+H_2OH\xrightarrow[heat]{H^+}RCOOH+R'OH$$



$$R-\overset{\overset{O}{\|}}{C}-NH_2 + H_2O \xrightarrow[H^+]{} RCOOH + NH_3$$



(4) From Grignard reagent

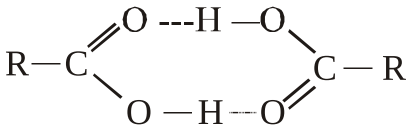


$$RMgX + CO_2 \xrightarrow{\text{Dryethier}} R-\overset{\overset{O}{\|}}{C}-OMgX \xrightarrow{H_3O^+} RCOOH + Mg(OH)X$$

Physical Properties

(i) Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature. The higher acids are waxlike solids.

(ii) Carboxylic acids have higher boiling point than aldehydes, ketones and even alcohols of comparable molcular masses. This is due to extensive association of carboxylic acid molecules through intermolecular hydrogen bonding and the acids exist as dimers.



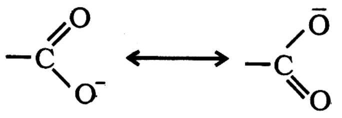
(iii) Simple aliphatic carboxylic acides upto 4 carbon atoms are soluble in water due to hydrogen bonding but higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part.

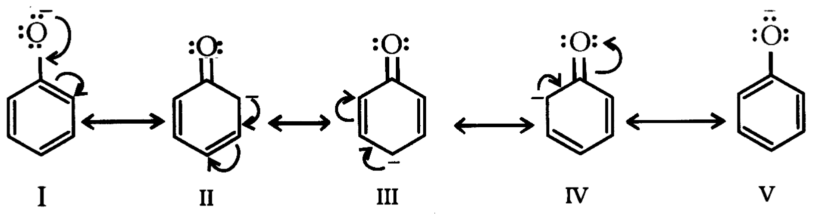
(iv) Benzoic acid is insoluble in water, but soluble in benzene, alcohol & chloroform etc.

Lecture - 81

Comparison of acid strength of carboxylic acids

1. Carboxyllic acids are weaker than mineral acids, but they are stronger than alcohols and many simple phenols.





The conjugate base of carboxylic acid is carboxylate ion, which is stabilized by two equivalent resonating structures, in which the negative charge is located on more electronegative oxygen atom.

On the other hand, the conjugate base of phenol is phenoxide ion, which is stabilized by three resonating structures in which the negative charge is located on less electronegative carbon atom. Therefore, the resonance in phenoxide ion is not as important as it is in carboxylate ion. Thus carboxylate ion is more stabilized than phenoxide ion, so carboxylic acids are more acidic than phenols.

2. Effect of substitutents on the acidity of carboxylic acids

Electron with drawing substituents increase the acidity of carboxylic acids by stabilizing the conjugate base through delocalisation of the negative charge by inductive and or resonance effects. Similarly electron donating substituents decrease the acidity by destabilizing the conjugate base.

Example :

The following acids are arranged in the order of decreasing acidity.

$CF_3COOH > CCl_3COOH > CHCl_2COOH > NO_2CH_2COOH$

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > HCOOH > C_6H_5COOH$

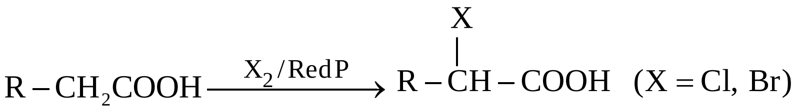
$C_6H_5COOH > CH_3COOH > CH_3CH_2COOH$

Chemical Properties of Monocarboxylic acids

$$R-COOH-\left|\begin{array}{ll}
\xrightarrow{\text{Na or NaOH}} & RCOONa+\frac{1}{2}H_2\\
\xrightarrow[\text{Conc.}H_2SO_4]{R^{/}OH,} & RCOOR^{/}+H_2O\\
\text{(Esterification)} & \\
\xrightarrow[P_2O_5]{RCOOH,\ \Delta} & (RCO)_2O\text{ Acid anhydride}\\
\xrightarrow{PCl_5\text{ or}, PCl_3\text{ or }SOCl_2} & R-COCl\\
\xrightarrow{NH_3} & RCOONH_4\xrightarrow[-H_2O]{\Delta}RCONH_2\\
\xrightarrow[\substack{\text{Reduction}\\ \text{(ii) }H_3O^+}]{\text{(i) }LiAlH_4/\text{Ether}} & RCH_2OH\\
\xrightarrow[\substack{\text{(ii) NaOH+CaO (Soda lime)}\\ \text{(iii) Heat}}]{\text{(i) Na}} & R-H+Na_2CO_3\\
\xrightarrow{\text{Na or K}} & RCOOK\xrightarrow[\text{Kolbe's electrolysis}]{\text{Electrolysis}}R-R\\
\xrightarrow[\text{Reduction}]{\text{HI and Red P}} & RH
\end{array}\right.$$

Halogenating carboxylic acid (Hell-Volhard - Zelinsky reaction)

Carboxylic acids having an $\alpha-$hydrogen atom are halogenated at the $\alpha-$position on treatment with Cl_2 or Br_2 in presence of small amount of red phosphorus to give $\alpha-$halo carboxylic acid.



$$R-CH_2COOH\xrightarrow{X_2/\text{Red P}}R-\underset{}{\overset{\overset{\Large X}{|}}{C}}H-COOH\quad (X=Cl, Br)$$

Distinction between formic acid and acetic acid

Formic acid reduces Tollen's reagent to form silver mirror and reduces Fehling solution to form a red precipitate of Cu_2O where as acetic acid does not. HCOOH easily oxidises to $CO_2 + H_2O$.

Hence a better reductant.

$$HCOOH + 2[Ag(NH_3)_2]OH \rightarrow CO_2 + 2H_2O + 2Ag + 4NH_3$$

Tollen's reagent

$$CH_3COOH \xrightarrow{\text{Tollen's reagent}} \text{No silver mirror}$$

$$HCOOH + 2Cu^{++} + 4OH^{-} \longrightarrow CO_2 + 3H_2O + Cu_2O$$

HOME ASSIGNMENT

1. (i) Between HCOOH and acetic acid, which more acidic and why ?

(ii) Arrange the following acids in the increasing order of acid strength

CH_3CH_2COOH, CH_3COOH, HCOOH

(iii) How will you prepare acetamide from aceticacid ?

(iv) What happens when sodium acetate is heated with sodalime.

(v) What do you mean by Hell- Volhard-Zelinsky reaction ? Give example.

Lecture - 82

Preparation and properties of benzoic acid

Preparation

1. From Grignard reagent (Phenyl magnesium bromide)

$$C_6H_5MgBr + CO_2 \rightarrow C_6H_5COOMgBr \xrightarrow{H_3O^+} C_6H_5COOH + Mg(OH)Br.$$

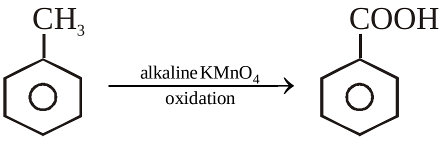
2. From phenyl cyanide.

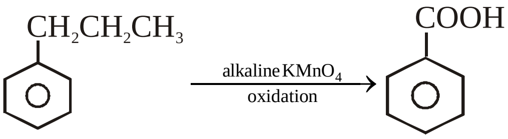
$$C_6H_5C \equiv N + H_2O \xrightarrow{H_3O^+} C_6H_5CONH_2 \xrightarrow{H_3O^+} C_6H_5COOH$$

3. From benzyl alcohol

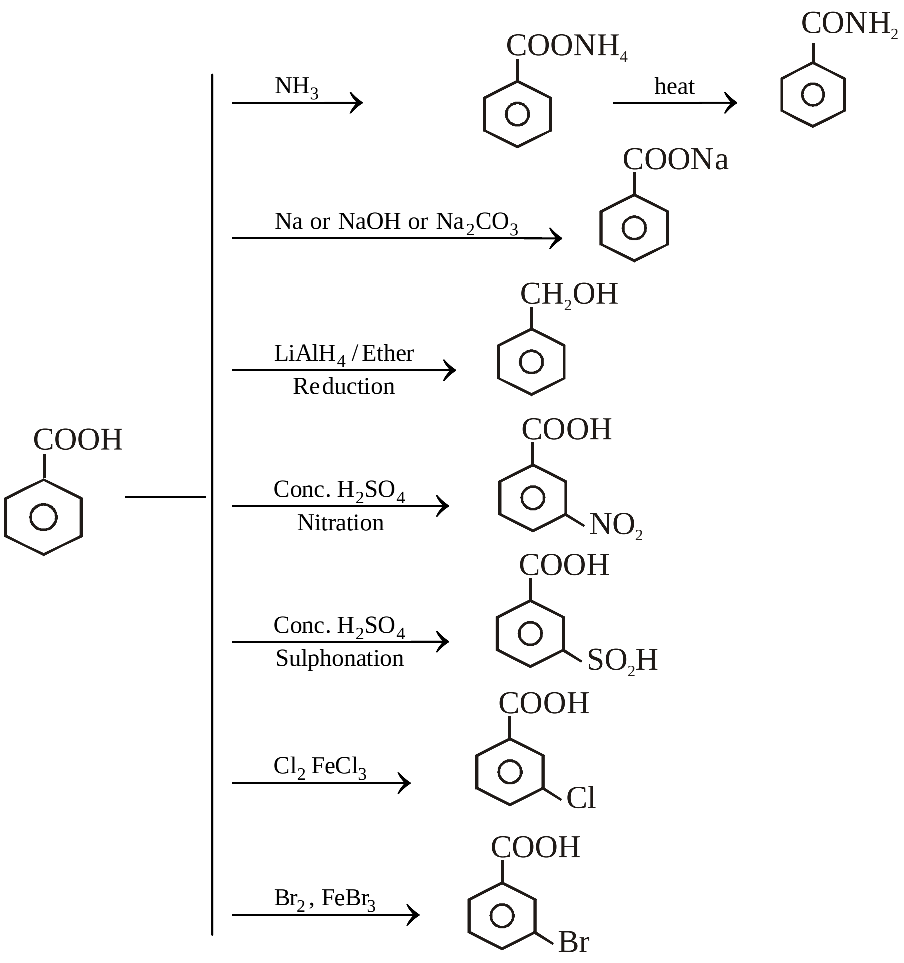
$$C_6H_5CH_2OH \xrightarrow{\text{Acidified } K_2Cr_2O_7} C_6H_5CHO \xrightarrow{\text{Oxidation}} C_6H_5COOH$$

4. **From alkyl benzene**





Properties



HOME ASSIGNMENT

(i) Give a method of preparation of benzoic acid from toluene.

(ii) How will you prepare benzyl alcohol from benzoic acid ?

(iii) How is benzoic anhydride prepared from benzoic acid.

(iv) Nitration of benzoic acid gives_________.

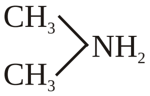
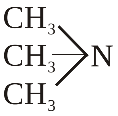
(v) $C_6H_5COOH \xrightarrow{NH_3} A \xrightarrow[\Delta]{} B \xrightarrow[\Delta]{P_2O_5} C \xrightarrow{H_2/Ni} D$. Identify A to D.

Lecture - 83

UNIT - XIII

(ORGANIC COMPOUNDS CONTAINING NITROGEN)

Aliphatic amines :- Amines are the derivatives of ammonia which are obtained by replacement of one, two or all the three hydrogen atoms by alkyl / or aryl groups.

		Common name	**IUPAC name**
Example -	$CH_3 - NH_2$	Methyl amine	methanamine
		Dimethyl amine	N-methyl methanamine
		Trimethyl amine	N,N-Dimethyl methanamine
	$C_6H_5NH_2$ ——	Aniline	Benzenamine

Preparation

1. By reduction of nitrocompounds

$$RNO_2 + 6H \xrightarrow[\text{Reduction}]{S_n+\text{Conc.HCl}} RNH_2 + 2H_2O$$

2. Ammonolysis of alkylhalide gives mixture 1^0, 2^0, 3^0 amino and quaternary ammonium salt.

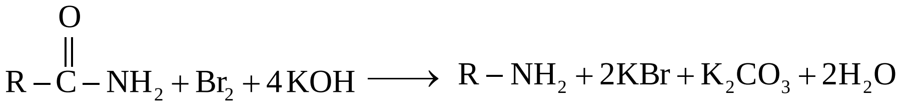
$$RX + RNH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4N^+X^-$$

3. By reduction of nitrites

$$R - C \equiv N \xrightarrow{H_2/Ni} RCH_2NH_2 \ \ (\text{Na} / C_2H_5OH \text{ or } LiAlH_4 \text{– other reducing agent})$$

Reduction by sodium and alcohol is called Mendius reaction.

4. **By Hofmann bromamide reaction :** The amine obtained has one carbon atom less than the corresponding amide.



$$R - \overset{\overset{\displaystyle O}{\|}}{C} - NH_2 + Br_2 + 4KOH \longrightarrow R - NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

5. From Grignard reagent :-

$$RMgX + ClNH_2(\text{chloramine}) \rightarrow RNH_2 + 2KBr + K_2CO_3 + 2H_2O$$

6. **From Carboxylic acid :-** Carboxylic acids react with hydrazoic acid to form primary amine. This reaction is called Schmidt reaction

$$R - COOH + N_3H \xrightarrow[\Delta]{H_2SO_4} RNH_2 + N_2 + CO_2$$

Basic Character of Aliphatic amines

The basicity of amines are due to the presence of unshared electron pair on nitrogen atom which accepts proton The amines behaves as Lewis base. Because of the basic nature of amines they react with mineral acids to form ammonium salts.

$$RNH_2 + HCl \rightarrow RN\overset{\oplus}{H_3}Cl^-$$

(i) Amines are stronger base than NH_3 due to +I effect of alkyl groups leading to high electron density or the nitrogen atom.

(ii) Due to electron releasing nature of alkyl groups (+I effect), the basic nature of aliphatic amines should increase with increase in the number of alkyl groups. This trend is folowed in gaseous phase. Hence the order of basicity of amines in gaseous phase is 3^0 amine > 2^0 amine > 1^0 amine > ammonia.

(iii) In aqueous solution the order of basicity is

2^0 amine > 1^0 amine > 3^0 amine > ammonia.

Reason - The basicity of an amine the aqueous solution primarily depends upon the stability of the ammonium cation formed by accepting proton from water. The stability of ammonium cation depends upon the following factors.

(i) +I - effect of the alkyl groups.

(ii) Extent of hydrogen bonding with water molecules

(iii) Steric effect of alkyl groups

(a) As the number of alkyl groups increases, the dispersal of the positive charge on the ammonium cation by the +I effect of alkyl groups increases. Hence on the basis of +I effect alone the basicity of amines should decrease in the order.

3^0 amine > 2^0 amine > 1^0 amine

(b) The stability of ammonium cation due to Hydrogen bonding depends upon the number of H-atoms present on the N-atom. Hence more is the number of H-atoms on N-atom. Hence more is the number of H-atoms on N-atom more stable is the ammonium cation. So the order of basicity should be 1^0 amine > 2^0 amine > 3^0 amine, which is opposite to the order of basicity by inductive effect.

(c) However in case of ammonium cation derived from 3^0 amines - there is same steric repulsion to H-bonding and hence stability further decreases. Thus on the basis of H-bonding and steric factors, the basicity of amines should decrease in the order 1^0 amine > 2^0 amine > 3^0 amine.

From the above discussion, we conclude that the combination of +I effect of alkyl groups, H-bonding and steric factors determine the stability of the ammonium cations in this solution. All these factors are favourable for secondary amine, so it is the strongest base.

If the alkyl group is small, like CH_{3^-} group, there is no steric hindrance to H-bonding. Hence stability due to +I effect of CH_{3^-} group, so 1^0 amine is stronger base that 3^0 amine. So the overall decrease in order of basicity of methyl amines is $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ (i.e. $2^0 > 1^0 > 3^0$)

How ever, when the alkyl group is bigger than $-CH_3$ group like $-C_2H_5$ group, their will be steric hindrance to H-bonding.

As a result stability due to +I effect predominates over the stability due to H-bonding, so 3^0 amine becomes more basic than 1^0 amine. Hence the overall decrease in order of basicity of ethylamines is $(C_2H_5)_2N > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ (i.e. $2^0 > 3^0 > 1^0$).

Lecture - 84 - 85

Properties of Aliphatic amines

Physical Properties

(a) Lower primary amines are gases, amines with 3 or more carbon atoms are liquids and higher ones are solids.

(b) Lower amines are soluble in water due to H-bonding with water molecules & solubility decreases with increase in molecular mass of amines due to increase in size of the hydrophobic alkyl part.

(c) The order of b.p is $1^0 > 2^0 > 3^0$ and it is due to intermolecular H-bonding.

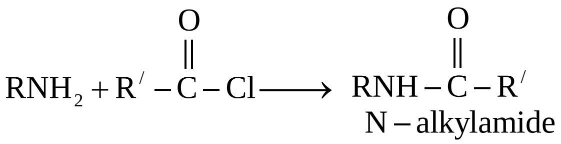
Chemical Propertion

(1) Alkylation of 1^0 amine results mixture 2^0, 3^0 and quaternary ammonium salt.

$$RNH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4N^+X^-$$

(2) Reaction with acid to form ammonium salt. $RNH_2 + HCl \rightarrow R\overset{\oplus}{N}H_3\,Cl^-$

(3) Reaction with acid chloride (Acylation).



$$RNH_2 + R' - \overset{\overset{\large O}{\|}}{C} - Cl \longrightarrow \underset{N-\text{alkylamide}}{RNH - \overset{\overset{\large O}{\|}}{C} - R'}$$

(4) Reaction with nitrous acid to give 1^0 alcohol.

$$R - NH_2 + HNO_2 \xrightarrow{\text{solid } NaNO_2 + \text{dil } HCl} ROH + N_2 + 3H_2O$$

(5) Carbyl amine reation -

$RNH_2 + CHCl_3 + 3KOH \rightarrow R - NC + 3KCl + 3H_2O$ (Alkylisocyanide/carbyl amine)

(6) Reaction with benzene sulphonyl chloride to give alkyl benzene sulphonamide wich is soluble in alkali. $R - NH_2 + C_6H_5SO_2Cl \rightarrow R - NH - SO_2C_6H_5 + HCl$

Preparation of Aniline

1. From nitrobenzene $C_6H_5NO_2 \xrightarrow[\Delta]{S_n + \text{Conc. } HCl} C_6H_5NH_2$

2. From phenol : $C_6H_5OH + NH_3 \xrightarrow[300^0C]{ZnCl_2} C_6H_5NH_2 + H_2O$

3. By Hofmann bromamide reaction.

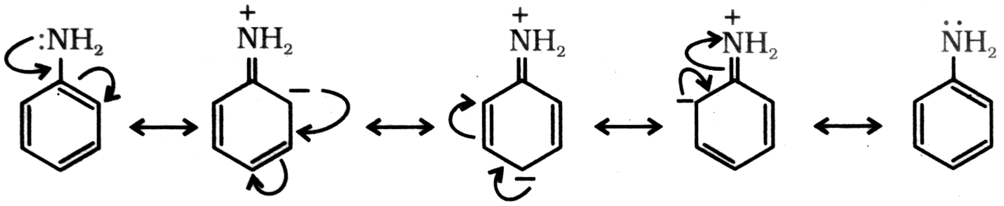
$$C_6H_5CONH_2 + Br_2 + 4KOH \rightarrow C_6H_5NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

4. From phenyl cyanide - $C_6H_5C \equiv N + 4H \xrightarrow[Na/C_2H_5OH]{LiAlH_4} C_6H_5CH_2NH_2$

Basic character of aniline

Aromatic amines are less basic than ammonia and aliphatic amines. The weaker basic character of aniline is explained below.

Due to resonance in aniline



I II III IV V

Due to resonance, the lone pair of electrons on the nitrogen atom gets delocalised over the benzene ring and thus is not available for protonation. Hence aromatic amines are less basic than ammonia.

Effect of substituents on the basicity of aromatic amines

Electron releasing groups like –OCH_3, –CH_3, increase basicity while electron with drawing groups like –NO_2, –SO_3H, –COOH, –CN, –X decrease the basicity.

Example : Basicity of p-toluedine > m-toluedine

Basicity of p-nitraniline < m-nitroniline

Aniline > m-nitroaniline > p-nitroaniline > o - nitroaniline

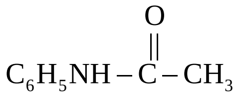
Propertion of Aniline

1. Reaction with CH_3I. (Methylation)

$$C_6H_5NH_2 + CH_3I \xrightarrow[-HI]{heat} C_6H_5NHCH_3 \xrightarrow{CH_3I\ heat} C_6H_5N\left(CH_3\right)_2 \xrightarrow{CH_3I,heat}$$

$$C_6H_5N^{\oplus}\left(CH_3\right)_3 I^-$$

2. Acetylation $C_6H_5NH_2 + CH_3COCl \xrightarrow{Pyridine}$



$$C_6H_5NH-\overset{\overset{\Large O}{||}}{C}-CH_3$$

(N – Phenyl ethanamide)

3. Benzoylation

$$C_6H_5NH_2 + C_6H_5COCl \xrightarrow{aq\ NaOH} C_6H_5NHCOC_6H_5 \text{ (N-phenylbenzamide)}$$

4. Carbylamine reaction

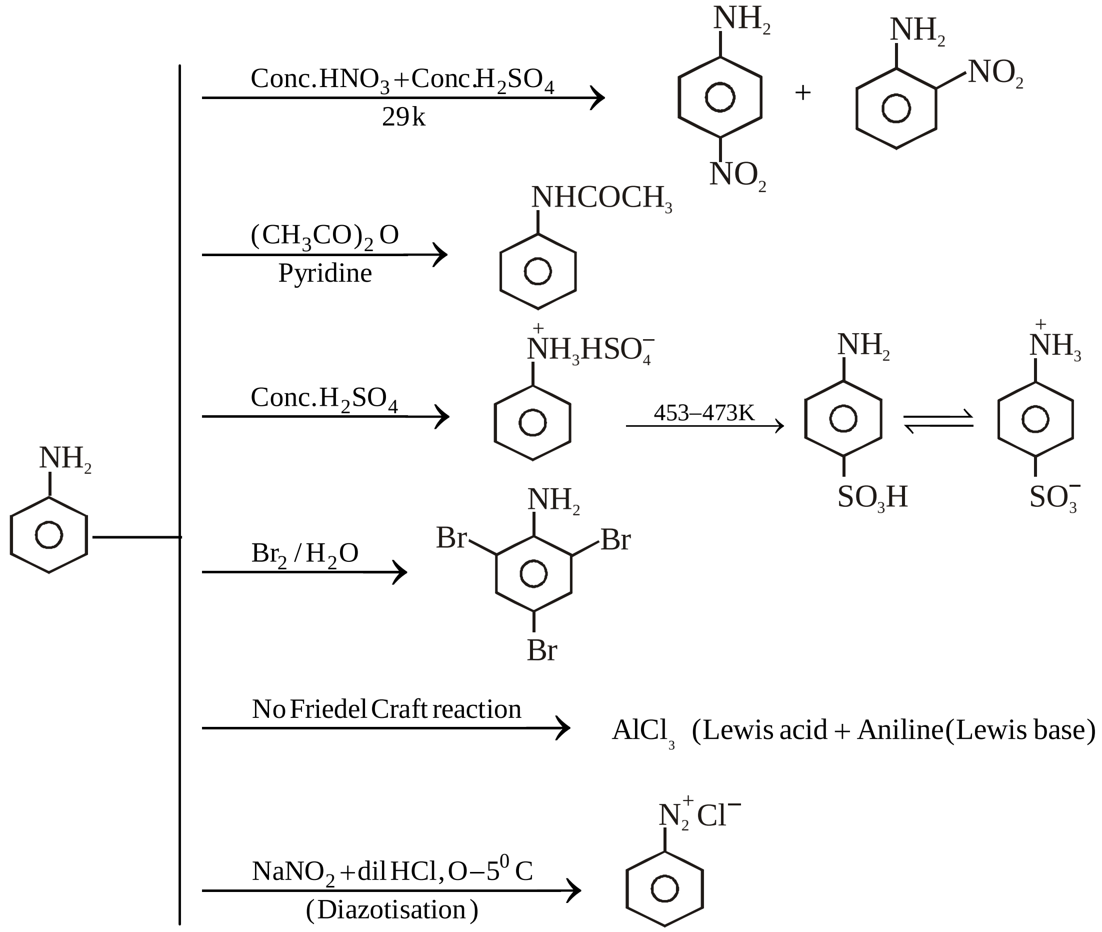
$$C_6H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_6H_5-N \overset{\rightarrow}{\equiv} C + 3KCl + 3H_2O$$

(Phenyl isocyanide / phenyl carbya min e)

5. Reaction with HNO_2

$$C_6H_5NH_2 + HNO_2 \xrightarrow[0-5^0C]{NaNO_2\ and\ dil\ HCl} C_6H_5\overset{\oplus}{N_2}Cl^- + NaCl + 2H_2O$$

Electrophilic substitution reaction of aniline



Lecture - 86

Preparation and properties of benzene diazonium chloride preparations

When aniline is treated with solid NaNO$_2$ and dil HCl at 273 – 278 K, benzene diazonium chloride is prepared.

$$C_6H_5NH_2 + HNO_2 + HCl \xrightarrow[273-278K]{\text{Solid } NaNO_2+\text{dil.}HCl} C_6H_5\overset{+}{N_2}Cl^- + 2H_2O$$

Properties

$$C_6H_5N_2Cl - \xrightarrow[\text{or } C_2H_5OH]{H_3PO_2,\ H_2O} C_6H_6$$

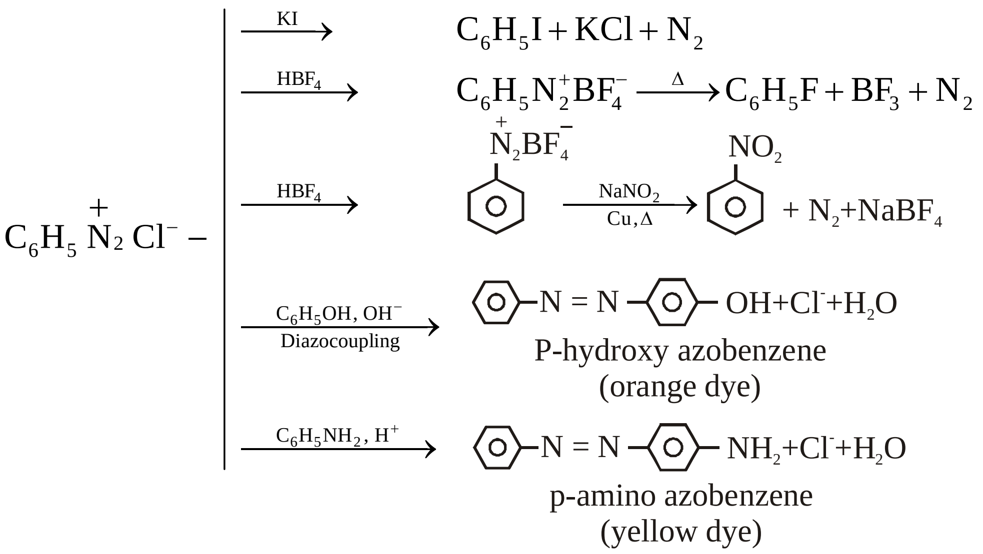
$$\xrightarrow{H_2O, 283K} C_6H_5OH$$

$$\xrightarrow[\text{Sandmeyer's reaction}]{Cu_2Cl_2, HCl} C_6H_5Cl + N_2$$

$$\xrightarrow[\text{Gattermann reaction}]{Cu, HCl} C_6H_5Cl + N_2$$

$$\xrightarrow{Cu_2Br_2,\ HBr} C_6H_5Br + N_2$$

$$\xrightarrow{CuBr+HBr} C_6 + H_5Br + N_2$$



$$C_6H_5\overset{+}{N}_2Cl^- \xrightarrow{KI} C_6H_5I + KCl + N_2$$

$$C_6H_5\overset{+}{N}_2Cl^- \xrightarrow{HBF_4} C_6H_5N_2^+BF_4^- \xrightarrow{\Delta} C_6H_5F + BF_3 + N_2$$

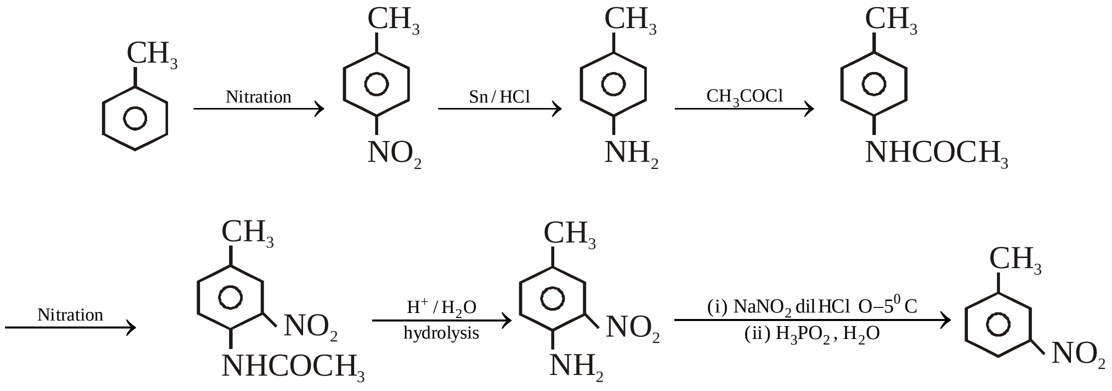
P-hydroxy azobenzene (orange dye)

p-amino azobenzene (yellow dye)

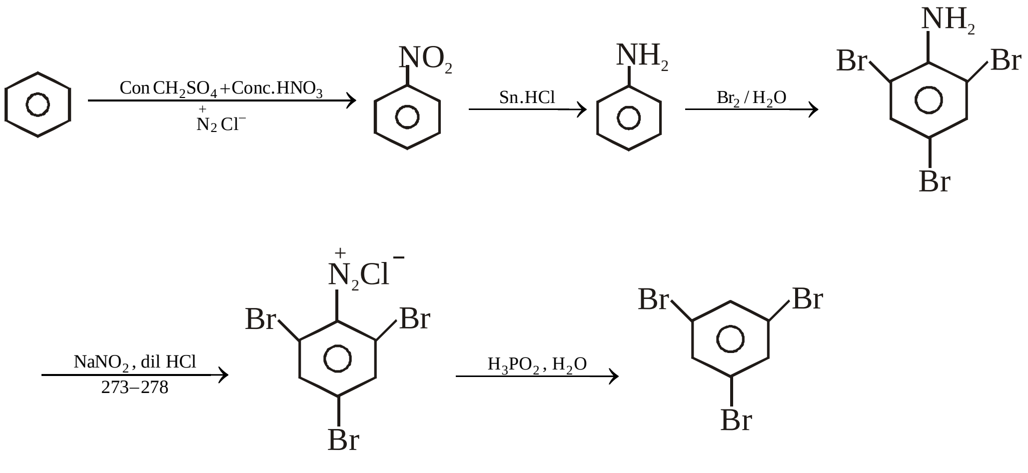
Lecture - 87

Interconversion of organic compounds :

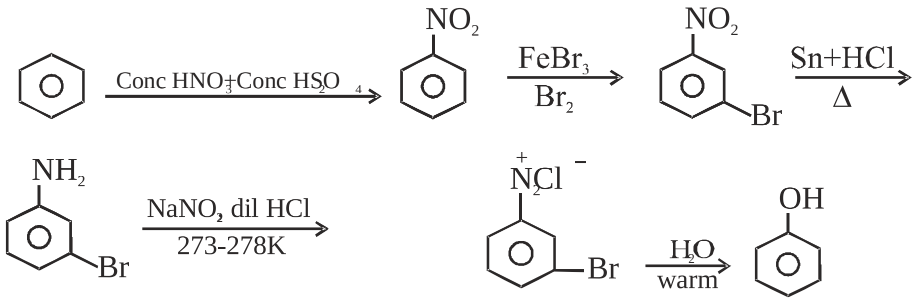
1) Toluene → metanitrotoluene



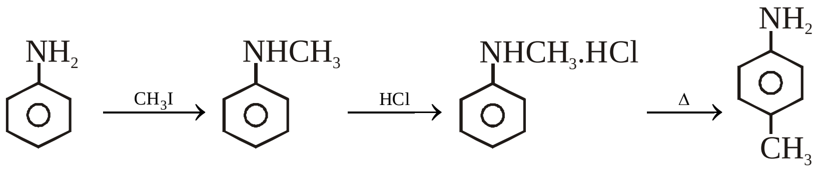
2) Benzene → 1, 3, 5- tribromo benzene



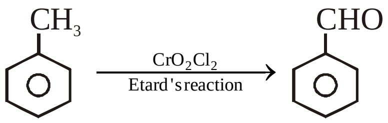
3) Benzene → m-bromophenol



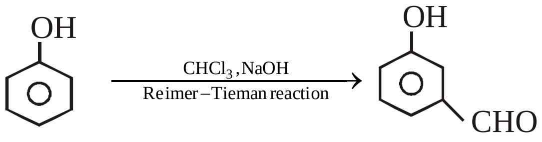
4) Aniline → p-toluidine



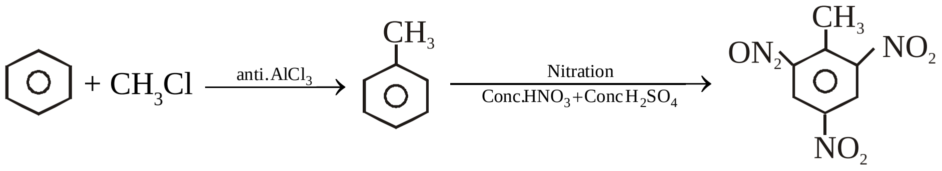
5) Toluene → benzaldehyde



6) Phenol → Salicylaldehyde

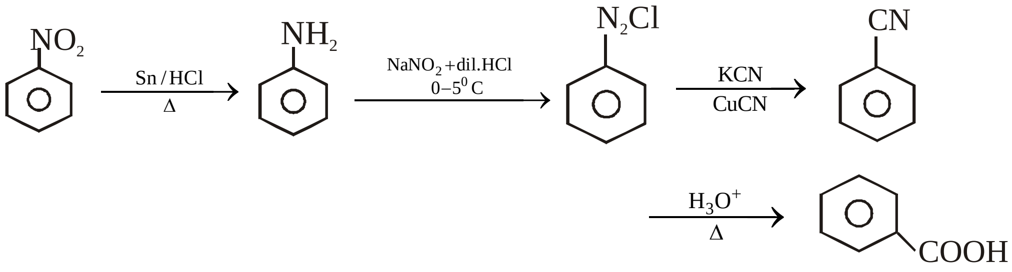


7) Benzene → TNT

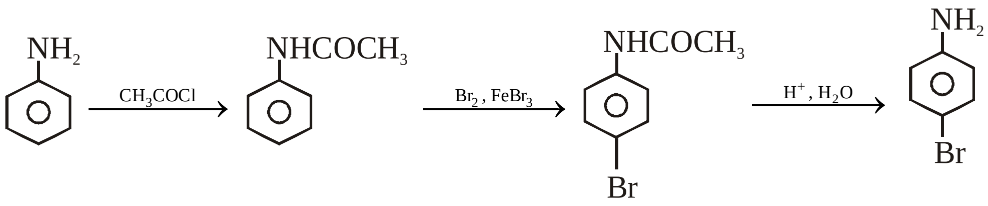


(3, 4, 6 - trinitrotoluene)

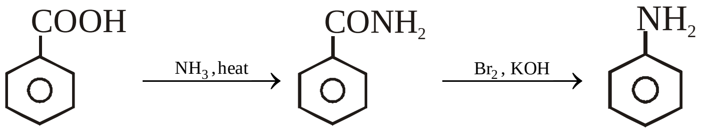
8) Nitrobenzene — benzoic acid



9) Aniline → p-bromoaniline

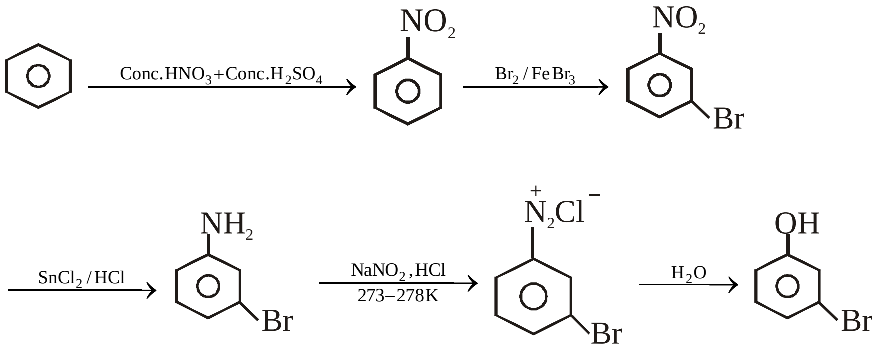


10) Benzoic acid to aniline



Hoffman bromamide reaction.

11) Benzene → m-bromophenol



12) Methanol → Ethanoic acid

$$CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow{KCN} CH_3CN \xrightarrow{H^+/H_2O} CH_3COOH$$

13) Ethanoic acid to methanamine

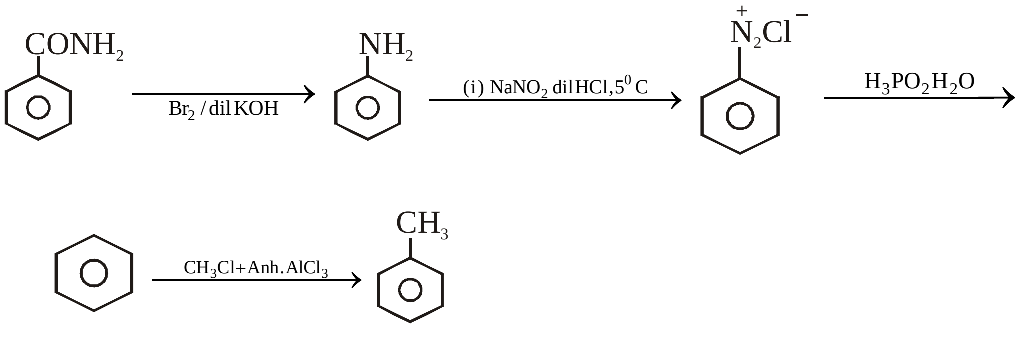
$$\left(CH_3COOH \longrightarrow CH_3NH_2\right)$$

$$CH_3COOH \xrightarrow[(ii)\ heat]{(i)\ NH_3} CH_3CONH_2 \xrightarrow{Br_2,KOH} CH_3NH_2$$

14) $C_2H_5OH \rightarrow CH_3COOH$

$$C_2H_5OH \xrightarrow{K_2Cr_2O_7,\ Conc.H_2SO_4} CH_3CHO \xrightarrow{oxidation} CH_3COOH$$

15) Benzamide to toluene



HOME ASSIGNMENT

1. Write what are A & B

(i) $C_6H_5NH_2 \xrightarrow[O-5^0\,C]{NaNO_2\,dil\,HCl} (A) \xrightarrow{H_3PO_2\,,H_2O} (B)$

(ii) $CH_3NH_2 \xrightarrow{Solid\,NaNO_2 + dil\,HCl} (A) \xrightarrow{PCl_5} (B)$

(iii) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{Br_2\,,H_2O} (B)$

2. Between CH_3NH_2 and $C_6H_5NH_2$, which is more basic.

3. How will you convert ethylcohol to acetaldehyde.

4. What is Reimer-Tiemann reaction

5. Work at following conversions :

$CH_3OH \longrightarrow CH_3–CH_2OH$

$CH_5CH_2OH \longrightarrow CH_3OH$

Propane-1-ol ⟶ propan-2-ol

$HCHO \longrightarrow CH_3CHO$

$CH_3CHO \longrightarrow HCHO$

$CH_3CHO \longrightarrow CH_3COCH_3$

$CH_3CHO \longrightarrow$ But-2-enal

$CH_3–CH_2–OH \longrightarrow$ butan-1-ol

$CH_3–CH_2–OH \longrightarrow$ But-1-yne

$HCOOH \longrightarrow CH_3COOH$

$CH_3COOH \longrightarrow HCOOH$

6. Privide the test to distinguish $CH_3CH_2NH_2$ from amiline.

Lecture - 88

UNIT - XIV

BIOMOLECULES

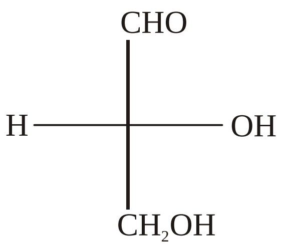
Carbohydrates - These include optically active polyhydric aldehydes or polyhydric ketones and large polymeric compounds that can be broken down into polyhydric aldehydes or ketones on hydrolysis. They are broadly classified into three groups.

– monosaccharides, oligo saccharides and polysaccharides.

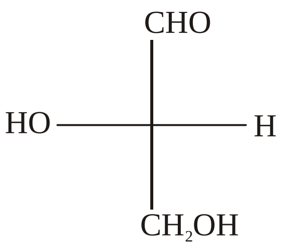
D and L - Configuration of glucose

The correct name of glucose is D–(+)–Glucose. since glucose is optically active, its enantiomer is L–(–)–glusose. The letter ‘D’ and ‘L’ are used before the name of glucose represent the configuration of –OH group at the penultimate (last butone) carbon atom of the carbon chain where as + or – sign within the bracket after the letter ‘D’ and ‘L’ refer to sign of rotation i.e., dextro rotatory or laevorotatory, respectively.

The meaning of D- and L– configuration is explained below.



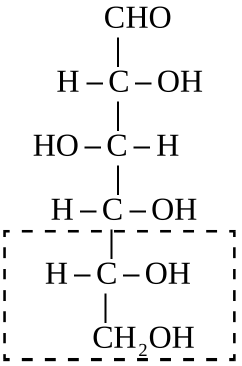
D-(+)-Glyceral dehyde



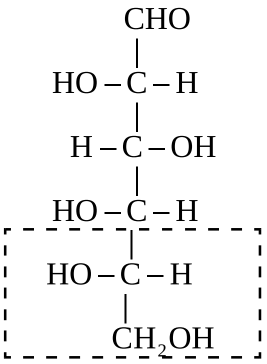
L-(-)-Glyceral dehyde

To assign D and L–configuration to monosaccharides, the simplest carbohydrate, glyceraldehyde is chosen as the standard. This is optically correlated to (+)–isomer of glyceral dehyde are assigned D-configuration, where as all those compounds which can be co related to (–)-isomer of glyceral dehyde are assigned L-configuration.

Thus, a monosaccharide like glucose and fructose is assigned D-configuration if the –OH group at the last chiral carbon, like that in D–(+)– glyceral dehyde lies towards right hand side. On the otherhand, it is assigned L-configuration if the OH-group on the last chiral carbon atom like that in L–(–)–glyceraldehyde lies on the left hand side.



D – (+) – glu cos e



L – (–) – glu cos e

Monosaccharides – These are simple sugars which cannot be hydrolysed to still simpler compounds. They are aldoses or ketoses. Example - Glucose, fructose.

Oligosaccharides – These are the carbohydrates which on hydrolysis give two to 10 molecules of the same or different monosaccharides on hydrolysis. Depending upon the number of monosaccharides obtained on hydrolysis they are classified as di, tri, tetrasaccharides.

(a) Disaccharides - sucrose, lactose, maltose
(b) Trisaccharides - Raffinose
(c) Tetrasaccharides stachyose.

Poly saccharides : These are the carbohydrates which on hydrolysis give a large number monosaccharides molecules.

Their general formula is $(C_6H_{10}O_5)_n$ where n = 100 to 3000

Example - Starch, Cellulose, protein, Glycogen.

Importance of carbohydrates

The main functions and uses of carbohydrates are as follows :

(a) Biofuels : Carbohydrates provide energy for the functioning of living systems and thus act as biofuels.

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + 2880\,\text{kJ}\,.$$

Glucose

Oxidation of glucose to carbon dioxide and water by a series of enzyme- catalysed reactions provide energy for functioning of cells.

(b) Reserve food material : The polysaccharides starch is the major reserve food material in plants. Glycogen, stored in liver and muscles act as the reserve food material in animals.

(c) Constituent of biomolecules : Two aldopentoses i.e., D–ribose and 2-deoxy-D-ribose are the essential components of RNA and DNA respectively.

(d) Structural material - The polysaccharides, cellulose, acts as the chief structural material of cell walls of bacteria and plants. Cellulose in the form of cotton is used for making clothes and cellulose in the form of wood is used for making furniture, doors, windows etc.

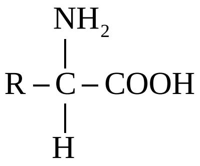
(e) Industrial material - Carbohydrates provide raw material for industries like textiles, paper and breweries.

Lecture - 89

Proteins - Proteins are a class of biolomecules essential for living beings. Chemically proteins are the condensation polymers (actually polyamides) in which the monomeric units are the α-amino acids.

$$\text{Proteins} \xrightarrow{\text{hydrolysis}} \text{peptides} \xrightarrow{\text{hydrolysis}} \alpha - \text{amino acids.}$$

α – amino acids : Amino acids contain omino–NH_2 and carboxyl (–COOH) as functional groups, when – NH_2 group is present on the α-position with respect to –COOH group, the amino acid is called α-aminoacid.

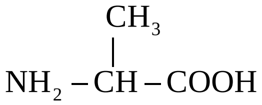


$$R - \overset{\overset{\displaystyle NH_2}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - COOH$$

(α-amino acid)

Example. Glycine ($NH_2\,CH_2COOH$)

alanine -



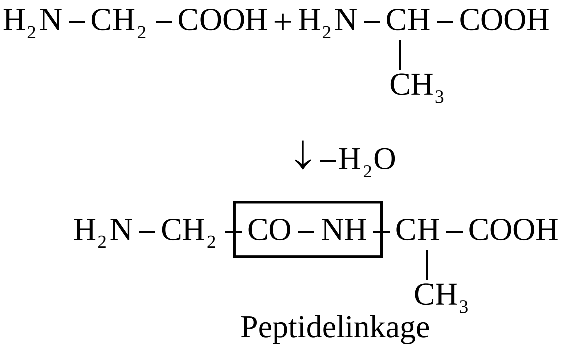
$$NH_2-\underset{}{\overset{CH_3}{\overset{|}{CH}}}-COOH$$

Essential and non-essential aminoacids

Out of 20 aminoacids required for protein synthesis, human body can synthesise only 10 aminoacids, which are called non-essential aminoacids. The remaining ten aminoacids which the human body can not synthesise are called essential amino acids.

Peptide bond or peptide linkage :-

Proteins are the polymers of α-aminacids and they are connected to each other by peptide bond. Chemically peptide bond is formed between –COOH group and –NH_2 group. The reaction between two molecules of similar or different amino acids proceeds through the combination of the amino group of one molecule and with the –COOH group of the other molecule. This results on the elimination of water and formation of a peptide bond –CO–NH–



$$H_2N-CH_2-COOH+H_2N-\underset{CH_3}{\underset{|}{CH}}-COOH$$

$$\downarrow -H_2O$$

$$H_2N-CH_2-\boxed{CO-NH}-\underset{CH_3}{\underset{|}{CH}}-COOH$$

Peptidelinkage

Polypeptide :- When 2, 3, 4 and 5 amino acids are linked, the respective products are called dipeptide, tripeptide, tetrapeptide and pentapeptide etc. But when the number of amino acids is more than ten, then the products are called **polypeptides.** A polypeptide with more than hundreed amino acid residues, having molecular mass higher than 10,000 is called a protein.

Structure of proteins The structure of proteins are usually discussed at four different levels i.e., primary, secondary, tertiary and quarternary structures.

(a) **Primary structure** The specific sequence in which the various α-amino acids present in a protein are linked to one another is called its primary structure.

The important of primary structure of a protein in determining its biological activity is shown by the fact that replacement of one aminoacid in the sequence of a protein destroys its biological activity. For example, replacement of one specific amino acid glutamic acid by valine in haemoglobin (the protein of bood), results in a disease called sickle cell anaemia.

(b) Secondary Structure : The conformation which the polypeptide chains assume as a result of hydrogen bonding is called secondary structure of protein. Two different secondary structures are possible.

(i) **α-Helix structure –** If the size of the R–groups is quite large, the H-bonds (intramolecular) are formed between the C=O of one amino acid residue and N–H of the fourth amino acid residue in the chain. This causes the polypeptide chain to coil up into a spatial structure called right handed α-helix structure. The α-helix is also known as 3.6_{13} helix, since each turn of the helix has approximately 3.6 amino acids and a 13-membered ring is formed by H-bonding.

Many fibrous proteins such as α-keratin in hair, nail, wool, skin, claws have α-helix structure.

b) **β-peated sheet structure -** In this conformation, the polypeptide chain & lie side by side in a Zig-Zag manner with alternate R groups on the same side situated at fixed distance apart. The two such neighbouring polypeptide chains are held together by intermolecular H-bonds.

(c) **Tertiary structure :** The tertiary structure of proteins represents overall folding of the polypeptide chains, i.e, further folding of the secondary structure.

(i) Fibrous proteins (example - α-keratin) have almost the same secondary (α-helix or β-pleated) structure through out the length of the protein.

In α-keratin, several α-helices are coiled about each other to form molecular ropes. So tertiary structure of fibrous proteins is rope like or rod-like.

(ii) In globular proteins, a part of the molecule may have the α-helical structure, while the other parts may have the β-pleted sheet structure. These different segments of the protein then fold to give a spherical shape to the entire molecule.

(d) **Quaternary structure :** Quaternary structure refers to the determination of no of subunit & their spatial arrangement with respect to each other in an aggregate protein molecule.

An exmaple of a protein containing a quaternary structure is haemoglobin. It is an aggregate of four polypeptide chains or sub units., two identical alpha chains (each containing 141 amino acid residues) and two identical beta chains (each containing 146 amino acid residues). These four subunits lie more or less at the vertices of a regular tetrahedron. Each polypeptide chain carries a heme group at its end.

Denaturation protein : In a biological system, protein with a unique three dimensional structure and biological activity is called a native protein. When a protein in its native form is subjacted to change of temperature or change in pH, the hydrogen bonds are disturbed. As a result of this globules unfold and helix gets uncoiled and protein loses its biological activity. This is called denaturation of protein. During denaturation 2^0 and 3^0 structures are destroyed but 1^0 structure remains intact.

Example- Boiling of egg, formation of chesse.

Enzymes Enzymes are biocatalysts. They are globular proteins. Enzymes are specific for a particular reaction for a particular substrate. (i) The enzyme for hydrolysis of maltose is maltase.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Maltase}} \underset{(\text{Glu}\cos\text{e})}{2C_6H_{12}O_6}$$

(ii)

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Invertase}} \underset{(\text{Glu}\cos\text{e})}{C_6H_{12}O_6} + \underset{(\text{Fuctose})}{C_6H_{12}O_6}$$

Lecture - 90

HORMONS

Hormones are a group of biomolecules which are produced in the ductless (endocrine) glands and are acrried to different parts of the body by the blood stream where they control various metabolic processes.

Some hormones, with their sources and function are given below.

Hormone	Source	Function
Adrenalin	Adrenal medula	Release glusose from glycogen, increases pulse rate and blood pressure
Testosterone	Testis	Normal function of male sex organ
Estrone or Estradiol	Ovary	Normal functioning of female sex organ
Insulin	Pancreas	Metabolism of glucose
Pituitary hormone	Pituitary gland	Stimutes thyroid gland testis, overy and mammary glands

VITAMINS

Vitamins are organic compounds which are required in small amounts in our diet but their deficiency causes dpecific diseases. Vitamins are of two types.

(i) **Fat soluble vitamins :** These vitamins are soluble in fat but insoluble in water. These are vitamin A, D, E and K. They are stored in liver.

(ii) **Water soluble vitamins :** These vitamins are soluble in water. These vitamins are supplied regularly in diet because they are readily secreted in unine and can not be stored except vitamin B_{12}.

Name of vitamins	Source	Deficiency diseases
1. Vitamin A	Fish, liver oil, carrots, butter and milk.	Xeroph thalmia (hardening of cornea of the eye)
2. VitaminB_1 (Thiamine)	Yeast, milk green vegetables	Beriberi
3. VitaminB_2 (Riboflavin)	Milk, egg White liver kidney.	Cheilosis (fissuring at corners of mouth and lips.
4. Vitamin B_6 (Peridoxine)	Yeast, milk, egg yolk cereals	Convulsions
5. Vitamin C (Ascorbic acid)	citrus fruits, amla and green leafy vegetables	scurvey
6. Vitamin D (Calciferol)	Exposure to sunlight, fish and egg yolk	Ricket, Osteomalacid
7. Vitamin E (α – Tocopherol)	Vegetable oils, like sunflower oil	Deficiency causes damage to reproductive system of both males and females
8. Vitamin K	Vegetable, fish, egg yolk & liver	It helps in coagulation of blood

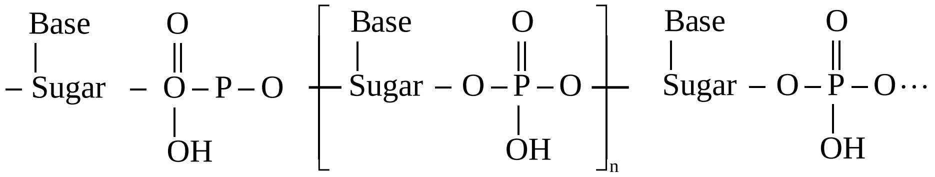
Lecture - 91

NUCLEIC ACID

The particles in the nucleus of the cell, responsible for heredity are called chromosomes which are made up of proteins and nucleic acid. These are mainly of two types) such as deoxy ribonuclei acid (DNA) and ribonucleic acid (RNA)

Chemical composition : Complete hydrolysis of DNA and RNA yields a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compounds called bases. In DNA molecules the sugar molecule is $\beta - \text{D} - 2 - \text{deoxy}$ ribose where as in RNA molecule it is $\beta - \text{D} - \text{ribose}$.

DNA contains four bases. These are adenine, guanine, cytosine and thymine. RNA also contains four bases, the first three bases are same as in DNA, but the fourth one is uracil.



$$-\overset{\overset{\text{Base}}{|}}{\text{Sugar}} - \underset{\underset{\text{OH}}{|}}{\overset{\overset{\text{O}}{\|}}{\text{O}}}-\text{P}-\text{O} \left[-\overset{\overset{\text{Base}}{|}}{\text{Sugar}} - \text{O}-\underset{\underset{\text{OH}}{|}}{\overset{\overset{\text{O}}{\|}}{\text{P}}}-\text{O}- \right]_n \overset{\overset{\text{Base}}{|}}{\text{Sugar}} - \text{O}-\underset{\underset{\text{OH}}{|}}{\overset{\overset{\text{O}}{\|}}{\text{P}}}-\text{O}\cdots$$

(A nucleic acid)

Deoxy ribonucleic acid (DNA)

(i) Primary structure . The sequency in which the four nitrogen bases are attached to the sugar-phosphate back bone of nucleic acid chain is called the primary structure of nucleic acid.

(ii) Secondary structure : DNA is composed of two strands of polynucleotides coiled around each other in the form of a double helix. The bases (specific pyrimidine groups) on one stand of DNA are paired with the bases (purine groups) on the other stands with the help of H-bonding. adenine (A) pairs with only thymine (T) via two hydrogen bonds while guanine (G) pairs with cytosine (C) through three H-bonds.

DNA - Finger Printing : Every individual has a unique finger prints which occur at the tips of the fingers. A sequence of bases on DNA is also unique for a person and information regarding this is called DNA finger printing.

DNA finger printing is now used

(i) in forensic laboratories for identification of criminals

(ii) to determine paternity of an individual

(iii) to identify the dead bodies in any accident by comparing the DNA of parents or children

(iv) to identify racial groups to rewrite biological evolution.

Ribonucleic acid (RNA) :- Complete hydrolys of RNA gives a pentose sugar phosphoric acid and nitrogen containing heterocyclic bases like adenine, guanine, Cytosine and uracil.

The primary structure of RNA corresponds to attachment of four nitrogen bases to sugar - phosphate back bone nucleic acid and in secondary structure of RNA, helices are present which are only 'single strand. stranded. Some times they fold back on themselves to form a double helix structure.

RNA molecules are responsible for translating coded message. They are of three types and they perform different functions. They are named as messager RNA (m-RNA), ribosomal RNA (r-RNA) and transfer RNA (t-RNA).

Biological functions of Nucleic acidics.

DNA is responsible for transmitting hereditary character and it is regarded as the reserve of genetic information. A DNA molecule undergoes self duplication during cell division and identical DNA strands are transferred to daughter cells. Another important function of nuclei acid is protein synthesis in the cell. Actually proteins are synthesised by various RNA molecules in the cell but the message for the synthesis of a particular protein is present in DNA.

HOME ASSIGNMENT

1. (a) Name the Nitrogen bases present in RNA.

(b) Which bond is present in peptides ?

(c) Which sugar molecule present in RNA is _______ .

(d) The process of conversion of milk to cheese is called _________ of protein.

(e) The enzyme that converts sucrose into glucose and fructose is ______.

(f) Which hormone regulated the function of male sex organ ?

(g) Give an example of an oligo saccharide.

(h) Give the general formula of starch.

(i) What is the position of – OH group on C-5 carbon atom in D–(+) –Glucose.

(j) What are the products obtained by oxidation of glucose in the biosystem ?

(k) Which carbohydrate is present is liver that stares glucose ?

(l) What isthe hydrolysis product of maltose and which enzyme is responsible for this hydrolysis ?

(m) Write the structure of two α-amino acids.

(n) What are essential and non-essential amino acids?

(o) What is the primary structure of protein ?

(p) Which structure are destroyed during denaturation of proteins ?

(q) Name the hormone that stimulate the thyroid gland ?

Lecture - 92 & 93

UNIT - XV

(POLYMERS)

Polymers - Polymers are defined as large molecules having very high molecular mass and consists of a very large number of repeating structural units joined together through covalent bonds in a regular fashion.

Monomers - The simple molecules from which repeating structural units are derived are called monomers.

$$n\left(CH_2{=}CH_2\right) \xrightarrow{\text{Polymerisation}} \left(CH_2 - CH_2\right)_n$$

Ethene (Polythene)

A Classification of Polymers based on source

(i) Natural Polymers - The polymers found in nature i.e. the animals and plants are called natural polymers.

Example - Protein, silk, wool, starch, natural rubber.

(ii) Synthetic polymers - These are man made polymers like plastics (polythene, PVC), fibres (terylene, dacron) etc.

B. Classifiation based on the structure

(i) Linear polymer - In this the monomers join together to form long straight chain of polymer molecule.

Example - Polythene, nylon, polyster.

(ii) Branch Chain Polymer - In these polymers, the manomer units not only join to produce the linear main chain, but also form branches of differentlengths along the main chain.

Example - Starch, glycogen.

(iii) Cross-linked or three dimensional net work polymers

In this type of polymers the initially formed linear polymer chains are joined together to form three dimensional network structure.

Example - Bakelite, melamine

C. Classification based on repeating structural units

(i) Homopolymer - This type of polymers contain only one type of monomers.

Example -

$$n\left(CH_2{=}CH_2\right) \xrightarrow{\text{Polymerisation}} \left(CH_2 - CH_2\right)_n$$

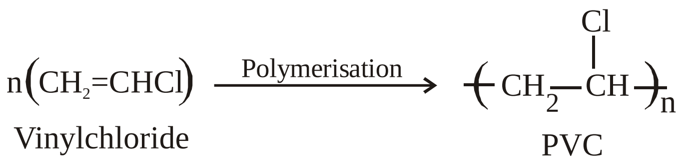
Ethene (Polythene)

(ii) Copolymer - Polymers having repeating structural units which are derived from two ro more different types of (Polymer of hexamethylene diamine and adipic acid).

Example - Nylon 6, 6.

D. Classfication based on mode of polymerization

(i) Addition polymers - These polymers are formed by the repeated addition of monomer molecules possessing double bonds without elimination of simple moleculese like water, HCl etc.



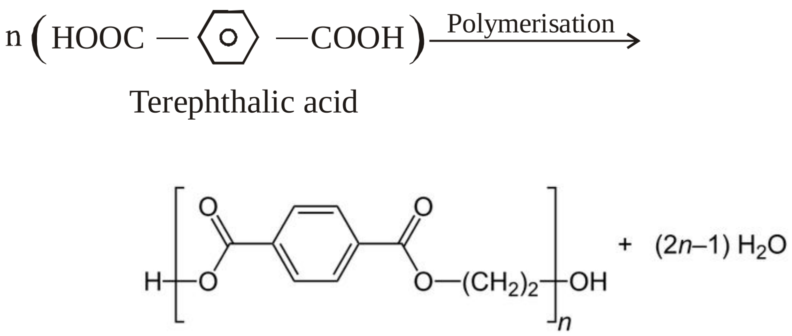
$$n(CH_2{=}CHCl) \xrightarrow{\text{Polymerisation}} \left(CH_2 - \underset{}{\overset{\overset{\large Cl}{|}}{CH}} \right)_n$$

Vinylchloride PVC

(ii) **Condensation Polymers -** These polymers are formed by the condensation of monomers containing polyfunctional groups with the elimination of simple molecules like H_2O, NH_3, HCl etc.

$$n(HO-CH_2-CH_2-OH) \quad +$$

(Ethylene glycol)



Terephthalic acid

(iii) **Copolymerisation -** A polymer consisting of two or more chemically different types of monomer units in the chain is called co-polymer and the process of polymerisation is called copolymerisation.

Example - 1, 3-butadiene and styrene form copolymer.

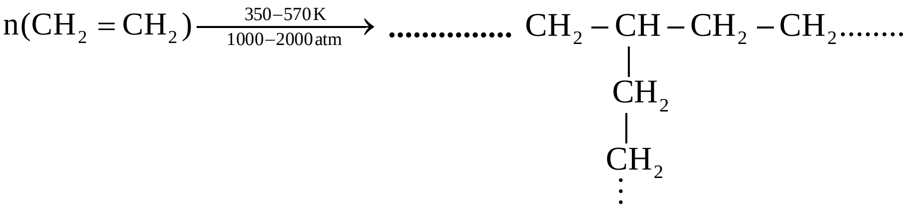
$$CH_2=CH-CH=CH_2+C_6H_5-CH=CH_2 \rightarrow$$

$$-CH_2-CH=CH-CH_2-\underset{\underset{\large C_6H_5}{|}}{CH}-CH_2-$$

IMPORTANT POLYMERS

1. Polythene :

(a) **Low density polythene** - It is manufactured by heating pure ethylene to 350 - 570k under pressure of 1000-2000 atmosphere in presence of trace of oxygen or peroxide.



$$n(CH_2=CH_2)\xrightarrow[1000-2000\,\text{atm}]{350-570\,K} \ldots\ldots\ldots\ldots\ CH_2-\underset{\underset{\underset{\underset{\vdots}{CH_2}}{|}}{\underset{CH_2}{|}}}{CH}-CH_2-CH_2\ldots\ldots\ldots$$

Uses :-

- (i) Packing material
- (ii) Insulating wires and cables
- (iii) Manufacture of toys, flexible pipes.

(b) **High density polythene :-** It is prepared when ether is heated to 330 - 350k under a pressure of 6-7 atmosphere in the presence of a catalyst consisting of triethyl aluminium and titanium tetrachloride (Ziegler - Natta catalyst)

$$n\left(CH_2 = CH_2\right) \xrightarrow[\text{Z.N.Catalyst}]{330-350\text{K},\,6-7\,\text{atm}} \left(CH_2 - CH_2 \right)_n$$

HDP

Uses :-

(i) Manufacture of buckets, dustbins, bottles

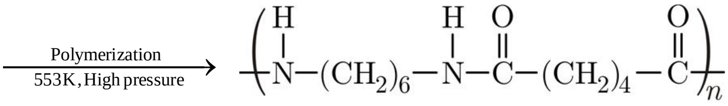
(ii) Manufacture of pipes

2. NYLON :-

(i) Nylon 6, 6 :-

$$n\ H_2N-\left(CH_2\right)_6-NH_2 \quad + \quad n\ HOOC-(CH_2)_4-COOH$$

(Hexamethylene dia min e) (Adipic acid)

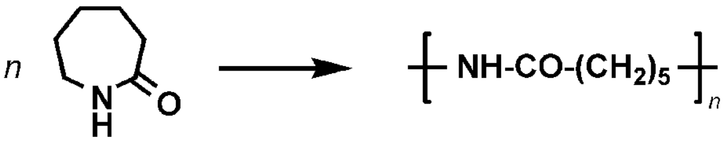


$$\xrightarrow[\text{553K, High pressure}]{\text{Polymerization}} \left(\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}} \right)_n$$

Nylon 66

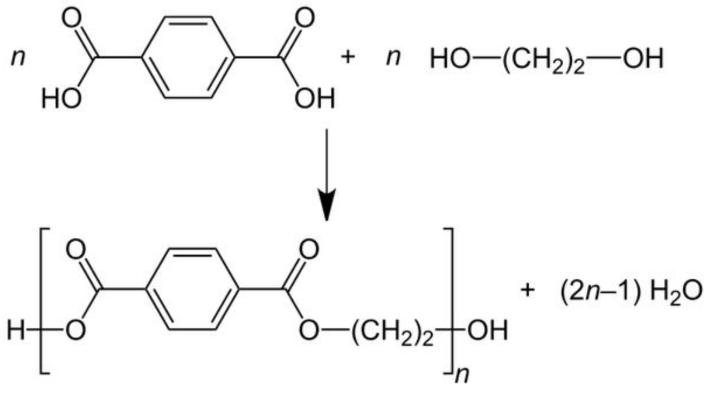
Use - Making tyre cord, fishing net s, bristles for brushes.

(ii) **Nylon - 6 :** Prepared by heating copralactam with water at high temperature 533 K.



3. Polyster

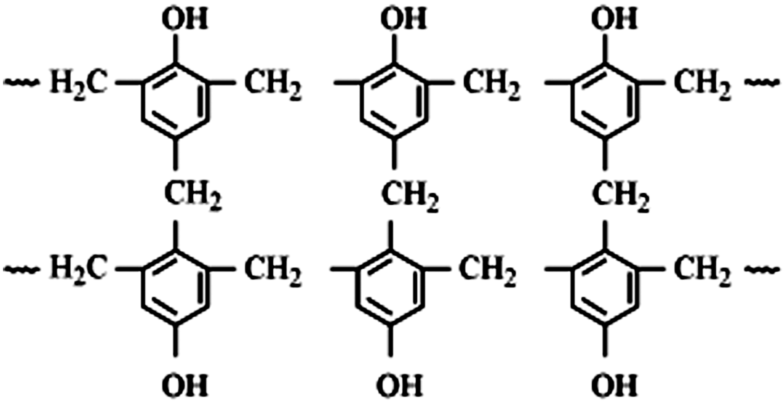
$$n\left(\text{Ethylene glycol} + \text{Terephthalic acid}\right) \xrightarrow[420-460\text{K}]{\text{Polymerisation}} \text{Polyster.}$$



4. **Bakelite :-** It is obtained by the condensation reaction of phenol with formaldehyde in presence of either an acid or base catalyst. The reaction starts with the initial formation of ortho and p-hydroxy methyl phenol derivatives, which futher react with phenol to form compounds having rings joined to each other through $-CH_2-$

groups. The initial product could be a linear product called Novolac, which is used in paints. Novolac on heating with formaldehyde undergoes cross linking to form an infusible solid mass called bakelite.

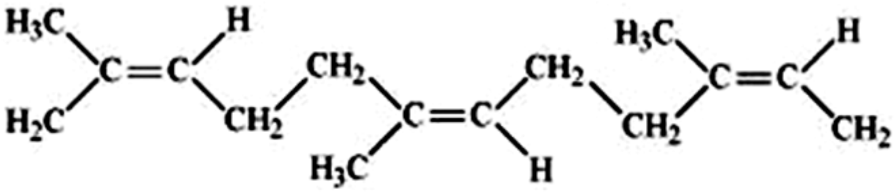
Use - For making comb, phonograph records, electrical switches, handles of various utensils.



Bakelite

5. Rubber -

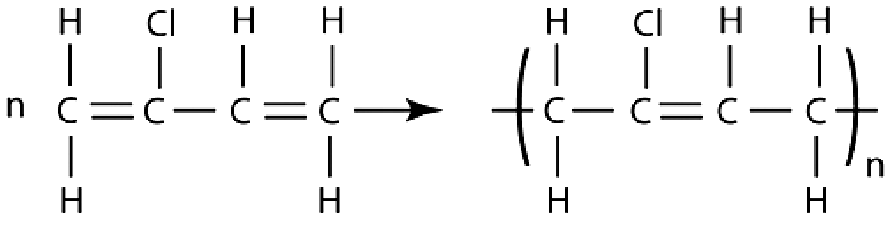
(a) Natural rubber, it is linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called as Cis- 1, 4 - polyisoprene.



Natural rubber

(b) Synthetic rubber - These are homopolymers of 1, 3- butadiene derivatives or copolymer of 1, 3 - butadiene or its derivatives with another unsaturated monomer.

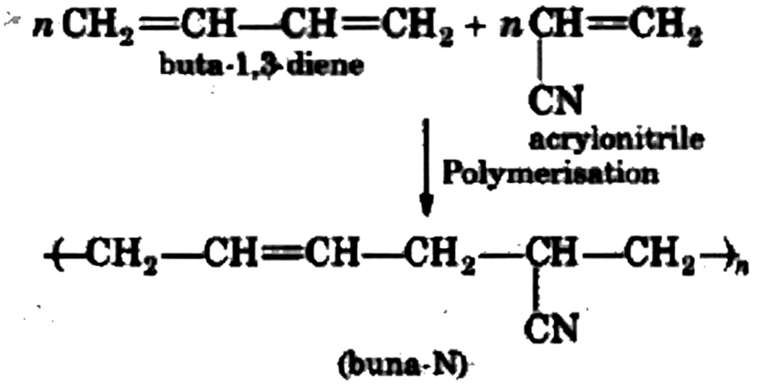
(i) Neoprene :- It is obtained by free radical polymerisation of chloroprene.



Chloroprene Neoprene

Use - Manufacture of conveyor belts, gaskets and hoses.

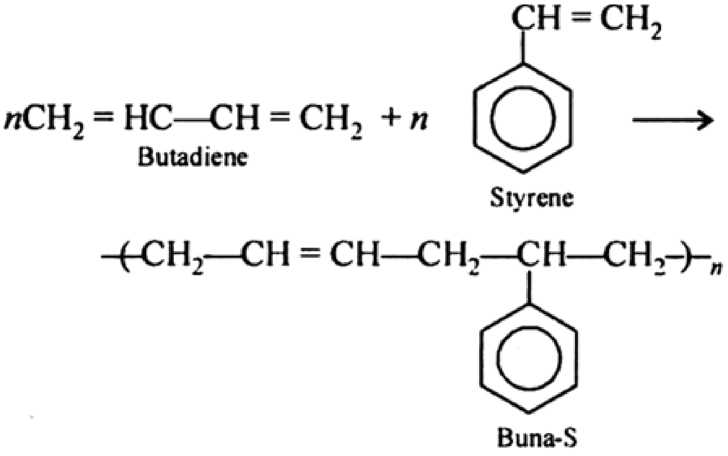
(ii) **Buna - N :-** It is obtained by copolymerization of 1, 3-butadiene and acrylonitrile in presence of peroxide catalyst.



$$n\,CH_2=CH-CH=CH_2 + n\,\underset{\displaystyle CN}{CH}=CH_2 \xrightarrow{\text{Polymerisation}} -\!\!(CH_2-CH=CH-CH_2-\underset{\displaystyle CN}{CH}-CH_2)\!\!-_n$$

Use - (i) It is resistant to action of petrol, lubricating oils, and organic solvents (ii) Used in making oil seeds, tank lining etc.

Buna - S :- It is a copolymer of 1, 3-butadiene and styrene.



Uses - Manufacture fo automobile tyres, rubber soles, water proof shoes, belts etc.

Biodegradable and Non-biodegradable polymers

Natural polymers (cellulose, starch, proteins, nucleic acids) disintegrate themselves during a certain period of time and hence are called biodegradable. On the other hand the synthetic polymers do not disintegrate by themselves over a period of time and hence are called non-biodegradable. The non-biodegradable polymers cause acute environmental problems.

Some biodegradable synthetic polymers are given below

1. **Poly β - hydroxy butyrate - co- β - hydroxy valerate (PHBV)**

It is obtained by the copolymerisation of 3-hydroxy butanoic acid and 3-hydroxy pentanoic acid.

Uses - It is used in orthopaedic devices and in controlled release of drugs.

2. **Nylon-2-Nylon-6 -** It is an alternating polyamide copolymer of glycine (H_2NCH_2COOH) and amino caprolic acid ($H_2N(CH_2)_5COOH$)

HOME ASSIGNMENT

1. Define the term polymerization.
2. Explain the term copolymerisation and give an example.
3. What are monomers of Nylon-6 and Nylon 6, 6.
4. Write the name of two biodegradable polymers.
5. What are the monomers of (i) Buna-N (ii) Dacron (iii) Neophrene.
6. Whare the uses of bakelite and low density polythene.

Lecture - 94, 95 & 96

UNIT - XVI

Chemistry in Everyday Life

A) **Chemicals as Medicine**

Drugs are chemicals of low molecular mass.

(a) **Analgesis :-** Analgesis are the drugs which reduce or abolish pain without causing impairment of consciousness, mental confusion, incordination, paralysis or some other disturbances of nerrous system. They are two types

(i) Non-narcotic analgesics - Example, Aspirin and paracetamol. Aspirin inhibits the synthesis chemicals known as prostaglandins which stimulate inflammation of tissue and cause par.

These drugs relieve skeletal pain due to arthritis, reduce fever (antipyretic), because of its anti blood clotting action, aspin is used for prevention of heart attack.

(ii) Narcotic analgesics - Example, Morphine, (codein are present in opium), heroin.

These analgesis are chiefly used for the relief of post operative pain, cardia pain and pains of terminal cancer and in child birth.

(b) **Antipyretics :-** Antipyretics are the chemicals used to bring down the body temperature during high fever.

Example :- Aspirin, paracetamol, phenocetin, novalgin, quinine.

(c) **Antiseptics :-** Antiseptics are the chemical substances (i.e. antibacterial) which prevent the growth of microorganisms and may even kill them. They are generally applied on living tissues such as wounds, cuts and diseased skin surface. Example - Furacin, soframycin, Detol (mixture of choroxylenol and terpineol), Bithionol, tincture iodine, iodoform, boricacid, mercruro chrome.

(d) **Disinfectant -** These are chemical substances (i.e. antibacterial) which kills micro-organisms but are not safe to be applied on living tissues. They are used to kill micro-organisms present in drains, toilets, floors etc.

Example - (i) 0.2% solution of phenol is antiseptic, but 1% solution of phenol in disinfectant.

(ii) Dettol (iii) Chlorine (0.2 to 0.4 ppm concentration) in aqueous solution (iv) sulphurdioxide. (v) Lysol (solution of erosol in soapy water)

(e) **Antibiotics -** Initially antibiotics were called chemical substances produced by microorganisms (bacteria, fungi and molds) that inhibit the growth or even destroy microorganisms. Now days, antibiotics refers to a substance produced wholly or partly by chemical synthesis, which in low concentration inhibits the growth or destroy microorganisms by intervening in their metabolic process.

The first discovered antibiotics is Penicillin and it was discovered by Alexander Fleming.

Types of anitbiotics

Bacterial	**Bacteriostatic**
Penicillin	Erythromycin
Strepto mycin	Tetra cycline
Ofloxacin	Chloro mphenicol

The antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are said to be broad spectrum antibiotics. But the antibiotics which are effective against Gram positive or Gram negative bacteria are called narrow spectrum antibiotics. If effective against a single organism or disease, they are called limited spectrum antibiotics.

Example - **Broad spectrum antibiotics** - Chlorom phenicol, tetracycline, vanocomycin, ofloxacin, Ampicillin, Amoxycillin

Narrow spectrum antibiotics - Penicillin G., Streptomycin is used for treatment of tuberculosis, Chloromphenicol for typhoid and pneumonia.

(f) **Antacids -** The substances which neutralise the excess acid and raise the pH to an appropriate level in stomach are called anticids.

Example - Sodium bicarbonate, magnesium hydroxide, aluminium hydroxide gel, ranitidine, cimetidine, magnesium trisilicate, omeprazole, lansoprazole.

(g) **Anti histamines :-** The hypersensitivity of some persons to some drugs, dust, pollen grains, a particular type of food or fabric etc. is called allergy and it is due to the release of a substance called histamine in the body.

Histamine causes allergy i.e. skin rashes, inflammatin of tissues, asthima, nasal congestion associated with common cold and allergic response to pollen.

The drugs which interfere with the natural action of histamine by competing with histamine for binding sites of receptor where histamine exerts its effect are called antihistamines or anti-allergic drugs.

Example - Brompheniramine, terfenadine cetrizine, diphenylhydramine (bendaryl) pheniramine maleate (avil), chloropheniramine, pomethazine.

(h) **Tranquilizers -** These are the drugs used for the treatment of stress, fatigue, mild and severe mental diseases and are also sleep producing.

Example - I proniazid, phenelzine (Nardil), Barbituric acid, veronal, luminal, seconal, amytal, chlordiazepoxide, meprobamate, equanil, valium and serotonin.

(i) **Antifertility drugs -** The chemical substances which are used to check pregnancy in women are called anti-fertility drugs or birth control pills or oral contraceptives.

Commonly used pills contain a mixture of norethindrone (a progesterone derivative) and novestrol or ethynylestradiol (an estrogen).

(j) Antimicrobials :- Drugs which are used to cure diseases caused by microbes or microorganisms such as bacteria viruses, fungi etc. are called antimicrobials. They include antibacterials, antifungals and anti-viral agents.

Example 0 Salvarsan is used for treatment of syphilis, prontosil, sulphanilamide, sulphapyridine. Antibiotics like ofloxacin, penicillon, tetracycline act as antibacterial drugs.

CHEMICALS IN FOOD

Chemicals are added to food for (i) their preservation (ii) enahncing their appeal and (iii) adding nutritive value in them.

(a) Aritificial Sweetening Agents :- The first popular artificial sweetening agent is saccharin (ortho-sulphobenzimide). It is 550 times as sweet as cone sugar and it is of great value to diabatic patients. Sum other artificial sweetening agents are aspartame, sucralose, alitame, cyclamate.

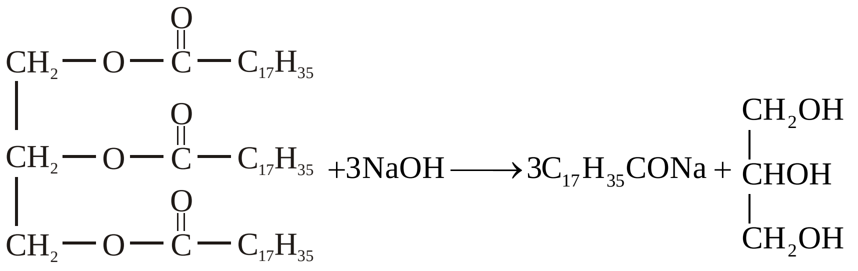
(b) Preservatives :- The chemical substances which are used to protect food against bacteria, yeasts and moulds are called preservations.

(c) Antioxidants :- Chemicals which are used to prevent oxidation of fats in processed foods such as potato chips, biscuits, breakfast cereals, crackers etc. are called antioxidants.

Example - Butylated hydroxy toluene (BHT), Butylated hydroxy anisole (BHA). Sulphurdioxide and $NaHSO_3$ which are used as preservatives also act as antioxidant for wine, bear, dried fruits, syrups etc. Ascorbic acid (Vitamin C) and tocopherols (Vitamin E) have also been used as antioxidants.

SOAPS AND DETERGENTS

SOAPS :- Soaps used for cleaning purposes are sodium or potassium salts of long chain fatty acids like oleic acid, stearic acid and palmitic acid. Soaps containing sodium salts are formed by heating fat (i.e. glyceryl ester of fatty acids) with aqueous sodium hydroxide. This reaction is called saponification.



$$\begin{array}{l}CH_2-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35}\\ |\\ CH_2-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35}\\ |\\ CH_2-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35}\end{array} +3NaOH \longrightarrow 3C_{17}H_{35}CONa + \begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}$$

Glyceryl ester of stearic acid (Fat) Glycerol

Advantages and disadvantages of using soap as cleaning agent

Soap is 100% biodegradable i.e. microorganisms present in sewage water can completely oxidise soap to CO_2 for which soap doesnot create any pollution problem. But the disadvantages are as follows.

(i) Soaps cannot be used in hard water since calcium and magnesium ions present in hard water produce curdy white precipitate of calcium and magnesium salts of fatty acids.

$$\underset{\text{Soap}}{2C_{17}H_{35}COONa} + CaCl_2 \longrightarrow \underset{\text{(Insoluble calcium stearate)}}{2NaCl + (C_{17}H_{35}COO)_2Ca}$$

These insoluble soap separate ass scum in water and hence a part of soap is wasted. Infact, this scum creates hindrance to good washing because it adheres to fibre of the cloth as gummy mass.

(ii) Soaps cannot be used in acidic solutions since acids present in the solution precipitate the insoluble free fatty acids which adhers to the fibre and thus reduce ability of soaps to remove oil and grease from fabrics.

Synthetic detergents :- Detergents are ammonium sulphones or sulphate salts of long chain sulphonic acids. Synthetic detergents can be used both in soft and hard water. These are of three types (i) Anionic detergents (ii) Cationic detergents and (iii) Non-ionic detergents.

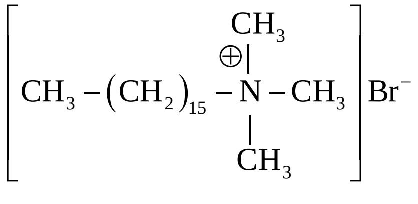
(i) Anionic detergents :- The sodium salts of sulphonated long chain alcohols are treated with conc. H_2SO_4 and the alkyl hydrogen sulphates thus formed are nutralized with alkali to form anionic detergents. Similarly alkyl benzene sulphanakes are obtained by neutralising alkyl benzene sulphonic acid with deal.

$$\underset{\text{Lauryl alcohol}}{CH_3(CH_2)_{10}CH_2OH} \xrightarrow{H_2SO_4} CH_3(CH_2)_{10}CH_2OSO_3H \xrightarrow{\text{Aq.NaOH}}$$

$$\underset{\text{sodium louryl sulphate}}{CH_3(CH_2)_{10}CH_2OSO_3^-Na^+}$$

In anionic detergent the anionic part of the molecule is involved in the cleaning action. Sodium salts of alkyl benzene sulphonates are important anionic detergents. They are used in house hold works ande also in tooth pastes.

(ii) Cationic detergents : In these detergents the major part of the molecules are cations and the cationic part of the molecule is involved in the cleaning action. These are quarternary ammonium salts (Chlorides, bromides, acetates) containing are or mole long chain alkyl groups.



$$\left[CH_3-(CH_2)_{15}-\overset{\overset{\displaystyle CH_3}{\oplus|}}{\underset{\underset{\displaystyle CH_3}{|}}{N}}-CH_3 \right] Br^-$$

Cetyl trimethyl ammonium bromide

Theis detergent is used in hair conditioners.

(iii) Non-ionic detergents - The detergents donot contain any ion in their constitution. These are actually esters of high molecular mass alcohols obtained from polyethylene glycol and stearic acid.

$$CH_3(CH_2)_{16}COOH + \underset{\text{Polyethylene glycol}}{HO(CH_2CH_2O)_nCH_2CH_2OH}$$

$$\longrightarrow \quad CH_3(CH_2)_{16}COO(CH_2CH_2O)_n CH_2CH_2OH$$

Polyethylene glycol stearate

Advantages of synthetic detergents over soap

(i) Can be used in hard water without any wastage while soups get wasted in hard water.

(ii) Can be used in acid medium while soaps get precipitated in acid medium.

Disadvantages of detergents :- As the hydrocarbon chain is highly branched, bacteria can not degrade them easily. Due to slow degragation of detergents, they accumulate in revers, ponds etc. These porsist in water even after sewage treatment and cause foaming in rivers, ponds and streans and their water gets polluted.

Now-a-days the branching of hydrocarbon chain is controlled and kept to minimum. Unbranched chains can be biodegraded more easily and then pollution is prevented.

Cleaninng action of soaps and detergents

The cleaning action of a soap or a detergent is called detergency.

All the soaps and detergents contain two characteristic groups.

(i) Non-polar hydrocarbon chain which is soluble in oil.

(ii) Polar end which is water soluble.

$$CH_3\underbrace{CH_2(CH_2)_{15}}_{\substack{\text{Non – polar end}\\ \text{(oil soluble)}}} \; - \; \underbrace{C-O^-Na^+}_{\substack{\text{polar end}\\ \text{(water soluble)}}} \quad \text{(Soap)}$$

$$\underbrace{CH_3-(CH_2)_{10}}_{\text{(oil soluble part)}}-CH_2 \; - \; \underbrace{OS_3^- Na^+}_{\text{(water soluble part)}} \quad \text{(Detergent)}$$

Cleaning action of soap takes place as follows :- The grease or oil sticks on the surface of cloth which contains dirt. When it comes in contact with soap solution, the sterate ions arrange themselves around it such away that the hydrophobic parts of the stearate ions go inside the oil (or grease) and the hydrophobic part projects outside the grease. As hydrophobic part is polar, these polar groups interact with the water molecules present around the oil or grease. As a result oil or grease is pulled away from the surface of the cloth into water to form ionic micelle which is then washed away with excess of water.

Similarly in case of detergents like sodium lauryl sulphate ($CH_3(CH_2)_{11}OSO_3^-N_2^+$), the polar group $SO_3^-N_2^+$ remains in water and the non polar end $CH_3(CH_2)_{11}$ entes inside the oil. When oil or grease is pulled away from the surface of the cloth into water ionic micelles which are formed are washed away by excess water.

HOME ASSIGNMENT

1. (i) Between sopa and detergent,____ is biodegradable.
   (ii) An example of antipyretic is_______.
   (iii) _____ is an example broad spectrum antibiotics.
   (iv) The first sweetening agent that was in use is______.
   (v) Ranitidine is used as_____.
2. (a) Which class of drugs are used in sleeping pills ?
   (b) What is the composition of birth control pill ?
   (c) Write the name of two antihistamines.
   (d) How does branching of hydrocarbon chain ?
   (e) What is the difference between disinfectant and antiseptic ?
   (f) Name a chemical which can be used both as disinfectant and antiseptic in different concentrations ?

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